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# MECHANISMS OF AMMONIA-SYNTHESIS REACTION REVISITED WITH THE AID OF A NOVEL GRAPH-THEORETIC METHOD FOR DETERMINING CANDIDATE MECHANISMS IN DERIVING THE RATE LAW OF A CATALYTIC REACTION

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Stoichiometrically exact, candidate pathways, i.e., mechanisms, for deriving the rate law of the catalytic synthesis of ammonia have been determined through the synthesis of networks of known elementary reactions constituting such pathways. This has been undertaken to reassess the validity of available mechanisms and to explore the possible existence of additional ones for the catalytic synthesis of ammonia. Synthesizing the networks of elementary reactions is exceedingly convoluted due to the combinatorial complexity arising from the fact the number of elementary reactions involved usually far exceeds that of available elementary balances, which is only 2 for the ammonia synthesis. Such a complexity can be circumvented by the rigorous and highly efficient, graph-theoretic method adopted in the present contribution. This method follows the general framework of a mathematically exact, combinatorial method established for process-network synthesis. It is based on a unique graph-representation in terms of process graphs (P-graphs), a set of axioms, and a group of combinatorial algorithms. The method renders it possible to generate with dispatch all feasible independent reaction networks, i.e., pathways, only once. The pathways violating any first principle of either stoichiometry or thermodynamics are eliminated. Moreover, the method is capable of directly generating rapidly the acyclic combinations of independent pathways.

**Keywords**: Ammonia synthesis, Reaction pathways, Mechanism, Networks, Identification, Synthesis, Algorithms, P-graph.

## Introduction

The mechanisms or pathways of the catalytic synthesis of ammonia from nitrogen and hydrogen, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, have been investigated intensively as well as extensively because of its long history, theoretical importance, and enormous economic implication. Nevertheless, the number of stoichiometrically exact mechanisms proposed as the candidates for deriving the rate law for this reaction increases continually as new computing methods are devised and additional elementary reactions are proposed [1-9]. The latter is probably attributable to the ever–enhancing sensitivity and accuracy of analytical instrumentation, in general, and spectroscopic instrumentation, in particular, for detecting active species; to the ever-enlarging variety of catalysts for increasing the yield [10]; and to the ever-expanding ranges of operating conditions for improving plant efficiency.

The determination of candidate mechanisms for deriving the rate law plays a key role in the study of the kinetics of catalytic reactions. Such mechanisms must be stoichiometrically exact [7, 11-14]. A reaction pathway, comprising the steps of elementary reactions, routes the precursors (starting reactants) of the reaction to the targets (final products) and vice versa; in other words, a reaction pathway signifies the mechanism of the reaction. The reaction pathway per se yields no information on the rate, reversibility, equilibrium, and extent of the reaction.

Any reaction pathway is in the form of a network of the steps of elementary reactions containing a loop or loops. In constituting a pathway, or network, each elementary reaction among plausible elementary reactions contributes the forward, reverse or no step to the network. As such, the possible combinations of these 3 possibilities that must be taken into account are

($3^{11}$-1) or 177,146 even if the network comprises only 11 elementary reactions. This can readily give rise to more than 100 plausible networks from which the feasible candidate pathways are to be identified; by any measure, this is a daunting task.

Difficulties involved in constructing networks of chemical reactions that can be the elementary reactions leading to the mechanism of a catalytic reaction are “the combinatorial explosion of the number of resultant networks, and the complexity involved in rendering a computer program to implement the algorithm for network construction effective both synthetically (from precursors towards targets) and retrosynthetically (from targets towards precursors)” [15, 16]. Substantial progress has been made to circumvent such difficulties mainly by resorting to various paradigms of linear algebra [1, 8, 11, 16-32]; nevertheless, much remains to be done.

The current contribution aims at reassessing the validity of available pathways or mechanisms of the catalytic synthesis of $NH_3$ and exploring if additional candidate pathways exist from the stoichiometric point of view. This is accomplished by resorting to a method of synthesizing a network of elementary reactions, corresponding to the pathway, i.e., mechanism, of a catalytic reaction [33]. This method, totally algorithmic in nature, has been developed by judiciously adapting the three available algorithms of the mathematically exact, graph-theoretic method for process-network synthesis. These algorithms are MSG for generating the maximal structure of the network, SSG for generating all the combinatorially feasible network structures, and ABB for determining optimal and near optimal networks. The method is firmly rooted in a set of axioms and expressed in the parlance of process graph or P-graph, in brief [34-39].

In reality, researchers in the field of catalysis have been remarkably successful in deriving the satisfactory rate laws for reactions of interest without having a complete set of stoichiometrically exact candidate mechanisms. This is mainly achieved through the judicious identification of plausible elementary reactions on the basis of spectroscopic measurements, which is frequently aided by energetic analysis of such elementary reactions. An expression for the rate law is usually derived by postulating, for simplification, the existence of the rate-controlling and equilibrium steps among the elementary reactions proposed. The final determination of the rate law is accomplished by fitting the resultant expression to the experimentally measured rate data [40-51]. More often than not, however, a multitude of stoichiometrically exact mechanisms emerges from a single set of plausible elementary reactions, some of which clearly resemble each other. Frequently, it is nearly impossible to discriminate statistically the rate laws derived from such mechanisms in the light of the experimental data. Hence, it would be highly advantageous to obtain a complete set of stoichiometrically exact candidate mechanisms prior to launching an effort for the rate-law determination. In fact, to do so would greatly facilitate the execution of such an effort because it exactly defines the boundary and limits its scope.

## Methodology

The current methodology for identifying the stoichiometrically complete mechanisms for a given overall reaction is based on the two sets of axioms, one being the set of 6 axioms of feasible reaction pathways and the other being the set of 7 axioms of combinatorially feasible networks, as well as on the graph representation of reaction steps in terms of P-graphs. In view of formal graph-theoretic description of the reaction-pathway identification problem (see Appendix 1), these axioms and P-graph representation give rise to the 3 combinatorial algorithms, including algorithm RPIMSG for the generation of the complete reaction network; algorithm RPISSG for the generation of the combinatorially feasible pathways; and algorithm PBT for the final determination of the feasible pathways.

```
inputs:  RPI problem $(E, M, O)$;
output: maximal structure $(m, o)$;

begin
    comment: reduction part of the algorithm;
    repeat
        $M := \Psi(O)$;
        $exc := \varnothing$;
        for all $x \in M$
        begin
            comment: Case 1
            if $x \notin \omega(E)$ and $\upsilon^{-}(x) = \varnothing$ then $exc := exc \cup \upsilon^{+}(x)$;
            comment: Case 2
            if $x \notin \omega(E)$ and $\upsilon^{+}(x) = \varnothing$ then $exc := exc \cup \upsilon^{-}(x)$;
            comment: Case 3
            if $x \notin \omega(E)$ and $|\upsilon^{-}(x)| = 1$ and $\upsilon^{+}(x) = X(\upsilon^{-}(x))$
                then $exc := exc \cup \upsilon(x)$;
            comment: Case 4
            if $x \notin \varpi^{-}(E)$ and $|\upsilon^{-}(x)| = 1$
                then $exc := exc \cup X(\upsilon^{-}(x))$;
            comment: Case 5
            if $x \notin \varpi^{+}(E)$ and $|\upsilon^{+}(x)| = 1$
                then $exc := exc \cup X(\upsilon^{+}(x))$;
        end;
        $O := O \setminus exc$;
    until $exc = \varnothing$;
    comment: composition part of the algorithm;
    $m := \varpi^{+}(E)$;
    $o := \varnothing$;
    repeat
        $add := \varphi^{-}(m) \setminus o$;
        $o := o \cup add$;
        $m := m \cup \Psi^{-}(o)$;
    until $add = \varnothing$;
    if $\varpi^{-}(E) \setminus m \neq \varnothing$ or $\varpi^{+}(E) \setminus m \neq \varnothing$
        then stop;
        comment: There is no maximal structure.
    write $(m, o)$;
end.
```

*Fig. 1.* Algorithm RPIMSG.

Monochloroacetic acid, ammonia solution and $Ca(OH)_2$ were purchased from Aldrich (Germany) and were used as received.

### *Axioms*

According to the classical chemical thermodynamics, the overall reaction and all elementary reactions in any mechanism are reversible, and each reaction step, either forward or reverse, is stoichiometrically exact [7, 11-14]. When a pathway leading from the starting reactants (precursors) to the final products (targets) is formed by selecting one or none of the steps of each elementary reaction, the complete mechanism is naturally recovered by supplementing the opposite step to each step of the pathway.

Moreover, the principle of microscopic reversibility prohibits the inclusion of any cycle in a pathway. The following set of 6 axioms of feasible reaction pathways can be formed from these first principles and conditions for any given overall reaction.

(R1) Every final product (target) is totally produced by the reaction steps represented in the pathway

(R2) Every starting reactant (precursor) is totally consumed by the reaction steps represented in the pathway.

(R3) Every active intermediate produced by any reaction step represented in the pathway is totally consumed by one or more reaction steps in the pathway, and every active intermediate consumed by any reaction step represented in the pathway is totally produced by one or more reaction steps in the pathway.

(R4) All reaction steps represented in the pathway are defined *a priori*.

(R5) The network representing the pathway is acyclic.

(R6) At least one elementary-reaction step represented in the pathway activates a starting reactant (precursor).

To focus on the combinatorial properties of the network comprising the feasible reaction pathways, the condition imposed by Axiom (R5) is relaxed except for the cycles formed by the forward and reverse steps of individual elementary reactions, and the condition imposed by Axiom (R6) is totally relaxed. Then, Axioms (R1) through (R5) can be recast as the seven axioms of the combinatorially feasible reaction networks, leading from the starting reactants (precursors) to the final products (targets) of any given overall reaction; this set of axioms is given in the following.

(T1) Every final product (target) is represented in the network.

(T2) Every starting reactant (precursor) is represented in the network.

```
input: reaction pathway identification problem ($E, O, M$)
output: all conbinatorially feasible structure ($m, o$)

begin
    PRISSG($\omega^+(E), \emptyset, \emptyset, \emptyset$);
end.

procedure PRISSG($p, dp, inc, exc$)
begin
    $exc$:=RPIRSG($exc$);
    if ($inc \cap exc \neq \emptyset$) then return;
    if $\omega^-(E) \setminus \Psi^-(O \setminus exc) \neq \emptyset$ or $\omega^+(E) \setminus \Psi^+(O \setminus exc) \neq \emptyset$
    then return;
    $inc$:=NX($inc, exc$);
    for all $x \in p$
        if ($\upsilon^-(x) \setminus exc \setminus inc = \emptyset$) then
        begin
            $dp := dp \cup \{x\}$;
            $p := (p \cup \Psi^-(\upsilon^-(x) \cap inc)) \setminus dp$;
        end;
    if $p = \emptyset$ then
    begin
        $o := inc$; $m := \Psi(o)$;
        print ($m, o$);
        return;
    end;
    let $x \in p$;
    $o_x := \upsilon^-(x) \setminus exc$;
    $o_{xb} := \upsilon^-(x) \cap inc$;
    $C := \wp(o_x \setminus o_{xb})$;
    if $o_{xb} = \emptyset$ and $x \notin \omega^-(E)$ then $C := C \setminus \{\emptyset\}$;
    for all $c \in C$
        RPISSG( $(p \cup \Psi^-(c \cup o_{xb})) \setminus (dp \cup \{x\}), dp \cup \{x\}$,
         $inc \cup c, exc \cup (o_x \setminus o_{xb} \setminus c) \cup X(c)$ );
end;
```

*Fig. 2.* Algorithm RPISSG and subsidiary algorithms.

```
function RPIRSG($exc$)
begin
    repeat
        $m := \Psi(O \setminus exc)$;
        $ex := \emptyset$;
        for all $x \in m$
        begin
            comment: Case 1
            if $x \notin \omega(E)$ and $\upsilon^-(x) \setminus exc = \emptyset$ then $ex := ex \cup \upsilon^+(x)$;
            comment: Case 2
            if $x \notin \omega(E)$ and $\upsilon^+(x) \setminus exc = \emptyset$ then $ex := ex \cup \upsilon^-(x)$;
            comment: Case 3
            if $x \notin \omega(E)$ and $|\upsilon^-(x) \setminus exc| = 1$
            and $\upsilon^+(x) \setminus exc = X(\upsilon^-(x) \setminus exc)$ then $ex := ex \cup \upsilon(x)$;
            comment: Case 4
            if $x \notin \omega^-(E)$ and $|\upsilon^-(x) \setminus exc| = 1$
                then $ex := ex \cup X(\upsilon^-(x) \setminus exc)$;
            comment: Case 5
            if $x \notin \omega^+(E)$ and $|\upsilon^+(x) \setminus exc| = 1$
                then $ex := ex \cup X(\upsilon^+(x) \setminus exc)$;
        end;
        $ex := ex \setminus exc$;
        $exc := exc \cup ex$;
    until $ex = \emptyset$;
    return $exc$;
end;
```

*Fig. 2.* (cont'd.).

```
function NX($inc$, $exc$)
begin
    repeat
        $m := \Psi(inc) \cup \omega(E)$;
        $in := \varnothing$;
        for all $x \in m$
        begin
            if $x \notin \omega^-(E)$ and $|\,\upsilon^-(x) \backslash exc\,| = 1$
                then $in := in \cup \upsilon^-(x) \backslash exc$;
            if $x \notin \omega^+(E)$ and $|\,\upsilon^+(x) \backslash exc\,| = 1$
                then $in := in \cup \upsilon^+(x) \backslash exc$;
        end;
        $in := in \backslash inc$;
        $inc := inc \cup in$;
    until $in = \varnothing$;
    return $inc$;
end;
```

*Fig. 2.* (cont'd.).

(T3) Each reaction step represented in the network is defined *a priori*.

(T4) Every active species represented in the network has at least one path leading to a final product (target) of the overall reaction.

(T5) Every chemical or active species represented in the network must be a reactant for or a product from at least one reaction step represented in the network.

(T6) A reactant of any elementary reaction represented in the reaction network is a starting reactant (precursor), if it is not produced by any reaction step represented in the network.

(T7) The network includes at most either the forward or reverse step of each elementary reaction represented in the network.

It is indeed worth noting that Axioms (T1) through (T7) straightforwardly reduce to Axioms (S1) through (S5) established for process-network synthesis [34-36]. The phrase, ''every active species,'' at the outset of Axiom (T4) can be replaced with the phrase, "any reaction step," since every active species generated by any reaction step is totally consumed by one or more of other reaction steps represented in the network.

## *P-Graphs*

The elementary-reaction steps are directed; thus, every network constituting a reaction pathway containing these steps can be represented by directed graphs, whereas such networks can not be uniquely represented by conventional graphs. The P-graphs, which are bipartite graphs, serve this purpose. In the P-graphs, the elementary-reaction steps are represented by horizontal bars; and the chemicals and active species, by circles. P-graph ($M$, $O$) representing a reaction network leading from the starting reactants (precursors) to the final products (targets) of the overall reaction of interest is *combinatorially feasible*, if it satisfies Axioms (T1) through (T7). Furthermore, P-graph ($M$, $O$) representing a reaction pathway is *feasible* if it also satisfies Axioms (R1) through (R6).

## *Algorithms*

The axioms naturally give rise to efficient algorithms necessary for carrying out the synthesis of a feasible network of elementary reactions; these algorithms are RPIMSG given in *Fig. 1* for generating the maximal networks; RPISSG given in *Fig. 2* for generating all the combinatorially feasible solution networks; and PBT given in *Fig. 3* for generating not only independent pathways but also the linear combination of such pathways, all of which are acyclic.

```
input: reaction pathway identification problem ($E$, $O$, $M$)
output: all feasible pathway ($m$, $o$)

begin
    PBT($\omega^+(E)$, $\omega^-(E)$, $\varnothing$, $\varnothing$, $\varnothing$, $\varnothing$);
end.

procedure PBT($p$, $c$, $dp$, $dc$, $inc$, $exc$)
begin
    $exc$:=RSG($exc$);
    if ($inc \cap exc \neq \varnothing$) then return;
    if $\omega^-(E) \backslash \Psi^-(O \backslash exc) \neq \varnothing$ or $\omega^+(E) \backslash \Psi^+(O \backslash exc) \neq \varnothing$
        then return;
    $inc$:=NX($inc$, $exc$);
    for all $x \in p$
        if ($\upsilon^-(x) \backslash exc \backslash inc = \varnothing$) then begin
            $dp := dp \cup \{x\}$; $p := (\, p \cup \Psi^-(\upsilon^-(x) \cap inc)\,) \backslash dp$; end;
    for all $y \in p$
        if ($\upsilon^+(y) \backslash exc \backslash inc = \varnothing$) then begin
            $dc := dc \cup \{y\}$; $c := (\, c \cup \Psi^+(\upsilon^+(y) \cap inc)\,) \backslash dc$; end;
    if $\exists(m, o)$ ($(m, o) \in avoid$, $o \subseteq inc$) then return;
    if $p = \varnothing$ and $c = \varnothing$ then begin
        $o := inc$; $m := \Psi(o)$;
        if $dp = dc$ and Solution( ($m$, $o$) ) then print ($m$, $o$);
        return;
    end;
    if ($inc \backslash sol \neq \varnothing$) or ($exc \backslash (O \backslash sol) \neq \varnothing$ ) or ($sol = \varnothing$)
        then $sol$=CandidateSolution( $inc$, $exc$);
    if ($sol = \varnothing$) then return;
    if $p \neq \varnothing$
        then let $x \in p$, where pFreedom($x$, $inc$, $exc$) is mininal;
    if $c \neq \varnothing$
        then let $y \in c$, where cFreedom($y$, $inc$, $exc$) is mininal;
    If $c = \varnothing$ or
    ($p \neq \varnothing$ and pFreedom($x$, $inc$, $exc$)<cFreedom($y$, $inc$, $exc$))
    then begin
        $o_x := \upsilon^-(x) \backslash exc$; $o_{xb} := \upsilon^-(x) \cap inc$; $C := \wp(o_x \backslash o_{xb})$;
        if $o_{xb} = \varnothing$ and $x \notin \omega^-(E)$ then $C := C \backslash \{\varnothing\}$;
        for all $q \in C$
            PBT( $(p \cup \Psi^-(q \cup o_{xb})) \backslash (dp \cup \{x\})$, $c$, $dp \cup \{x\}$, $dc$,
             $inc \cup q$, $exc \cup (o_x \backslash o_{xb} \backslash q) \cup X(q)$ );
    end;
    else begin
        $o_y := \upsilon^+(y) \backslash exc$; $o_{yb} := \upsilon^+(y) \cap inc$; $C := \wp(o_y \backslash o_{yb})$;
        if $o_{yb} = \varnothing$ and $y \notin \omega^+(E)$  then $C := C \backslash \{\varnothing\}$;
    for all $c \in C$
        PBT( $p$, $(c \cup \Psi^+(q \cup o_{yb})) \backslash (dc \cup \{y\})$, $dp$, $dc \cup \{y\}$,
         $inc \cup q$, $exc \cup (o_y \backslash o_{yb} \backslash q) \cup X(q)$ );
    end;
end;
```

*Fig. 3.* Algorithm PBT and subsidiary algorithms.

```
function CandidateSolution( inc, exc)
begin
    LP:
        $\forall_{e_i \in inc} \; v_i \geq 1$
        $\sum_{e_i \in O \setminus exc} v_i e_i = E$
        $\sum_{e_i \in o} v_i \rightarrow \min$
    if LP is not feasible
        then return $\emptyset$;
        else begin
            Solve LP;
            $sol := \{e_i: e_i \in O \setminus exc, v_i > 0\}$;
            return $sol$;
        end;
end;
```

*Fig. 3.* (cont'd.).

```
function Solution( (m, o) )
begin
    LP:
        $\forall_{e_i \in o} \; v_i \geq 1$
        $\forall_{e_i \in o} \; v_i \leq \frac{1}{\varepsilon^2}$
        $\sum_{e_i \in o} v_i e_i = E$
        $\sum_{e_i \in o} v_i \rightarrow \max$
    if LP is not feasible
        then return FALSE;
        else begin
            Solve LP;
            if $\forall_{e_i \in o} \left( v_i \leq \frac{1}{\varepsilon} \right)$
                then begin
                    $avoid := avoid \cup \{(m, \mathrm{X}(o))\}$;
                    return TRUE;
                end;
                else begin
                    $o := \left\{ e_i: v_i > \frac{1}{\varepsilon} \right\}$; $m := \Psi(o)$;
                    $avoid := avoid \cup \{(m, o), (m, \mathrm{X}(o))\}$;
                    return FALSE;
                end;
        end;
end;
```

*Fig. 3.* (cont'd.).

```
function pFreedom(x, inc, exc)
begin
    if $x \in \omega^-(E)$ or $\upsilon^-(x) \cap inc = \emptyset$
        then return $|\upsilon^-(x) \setminus inc \setminus exc|$
        else return $|\upsilon^-(x) \setminus inc \setminus exc| - 1$;
end;

function cFreedom(y, inc, exc)
begin
    if $y \in \omega^+(E)$ or $\upsilon^+(y) \cap inc = \emptyset$
        then return $|\upsilon^+(y) \setminus inc \setminus exc|$
        else return $|\upsilon^+(y) \setminus inc \setminus exc| - 1$;
end;
```

*Fig. 3.* (cont'd.).

*Table 1* List of Plausible Elementary Reactions

(1) $H_2 + \ell \rightleftharpoons H_2\ell$
(2) $H_2\ell + \ell \rightleftharpoons H\ell + H\ell$
(3) $N_2 + \ell \rightleftharpoons N_2\ell$
(4) $N_2\ell + \ell \rightleftharpoons N\ell + N$
(5) $N_2\ell + H_2\ell \rightleftharpoons N_2H_2\ell + \ell$
(6) $N_2H_2\ell + \ell \rightleftharpoons NH\ell + NH\ell$
(7) $N\ell + H\ell \rightleftharpoons NH\ell + \ell$
(8) $NH\ell + H\ell \rightleftharpoons NH_2\ell + \ell$
(9) $NH\ell + H_2\ell \rightleftharpoons NH_3\ell + \ell$
(10) $NH_2\ell + H\ell \rightleftharpoons NH_3\ell + \ell$
(11) $NH\ell + N\ell \rightleftharpoons N_2H\ell + \ell$
(12) $NH_2\ell + N\ell \rightleftharpoons N_2H_2\ell + \ell$
(13) $N_2H_2\ell + H_2\ell \rightleftharpoons N_2H_2\ell + N\ell$
(14) $NH_3\ell \rightleftharpoons NH_3 + \ell$

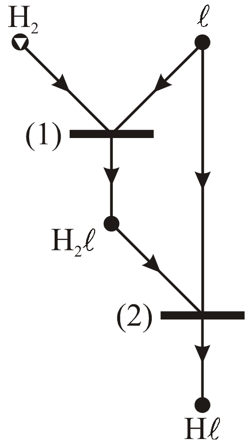

*Fig. 4.* P-graph representation of the network comprising the forward steps of elementary reactions (1) and (2).

The methodology presented above has been applied to two sets of available elementary reactions, one comprising elementary reactions (1) through (10) together with elementary reaction (14) in *Table 1*, and the other comprising elemenetary reactions (1) through (14) in the same table. For illustration, the P-graph of a network consisting of elementary reactions (1) and (2) is depicted in *Fig. 4*.

*Table 2* Independent Mechanisms Resulting from the First Set of Eleven Elementary Reactions

Mechanism 1
[3]
(1) $H_2 + \ell \rightleftharpoons H_2\ell$
(3) $N_2 + \ell \rightleftharpoons N_2\ell$
(5) $N_2\ell + H_2\ell \rightleftharpoons N_2H_2\ell + \ell$
(6) $N_2H_2\ell + \ell \rightleftharpoons NH\ell + NH\ell$
(9) $NH\ell + H_2\ell \rightleftharpoons NH_3\ell + \ell$
(14) $NH_3\ell \rightleftharpoons NH_3 + \ell\ell$

Mechanism 2
[2]
(1) $H_2 + \ell \rightleftharpoons H_2\ell$
(2) $H_2\ell + \ell \rightleftharpoons H\ell + H\ell$
(3) $N_2 + \ell \rightleftharpoons N_2\ell$
(4) $N_2\ell + \ell \rightleftharpoons N\ell + N$
(7) $N\ell + H\ell \rightleftharpoons NH\ell + \ell$
(8) $NH\ell + H\ell \rightleftharpoons NH_2\ell + \ell$
(10) $NH_2\ell + H\ell \rightleftharpoons NH_3\ell + \ell$
(14) $NH_3\ell \rightleftharpoons NH_3 + \ell$

Mechanism 3
[1, 7]
(1) $H_2 + \ell \rightleftharpoons H_2\ell$
(2) $H_2\ell + \ell \rightleftharpoons H\ell + H\ell$
(3) $N_2 + \ell \rightleftharpoons N_2\ell$
(4) $N_2\ell + \ell \rightleftharpoons N\ell + N$
(5) $N_2\ell + H_2\ell \rightleftharpoons N_2H_2\ell + \ell$
(7) $N\ell + H\ell \rightleftharpoons NH\ell + \ell$
(8) $NH\ell + H\ell \rightleftharpoons NH_2\ell + \ell$
(10) $NH_2\ell + H\ell \rightleftharpoons NH_3\ell + \ell$
(14) $NH_3\ell \rightleftharpoons NH_3 + \ell$

Mechanism 4
[8, 25]
(1) $H_2 + \ell \rightleftharpoons H_2\ell$
(3) $N_2 + \ell \rightleftharpoons N_2\ell$
(4) $N_2\ell + \ell \rightleftharpoons N\ell + N$
(7) $N\ell + H\ell \rightleftharpoons NH\ell + \ell$
(8) $NH\ell + H\ell \rightleftharpoons NH_2\ell + \ell$
(9) $NH\ell + H_2\ell \rightleftharpoons NH_3\ell + \ell$
(10) $NH_2\ell + H\ell \rightleftharpoons NH_3\ell + \ell$
(14) $NH_3\ell \rightleftharpoons NH_3 + \ell$

Mechanism 5
[8, 25]
(1) $H_2 + \ell \rightleftharpoons H_2\ell$
(3) $N_2 + \ell \rightleftharpoons N_2\ell$
(4) $N_2\ell + \ell \rightleftharpoons N\ell + N$
(5) $N_2\ell + H_2\ell \rightleftharpoons N_2H_2\ell + \ell$
(6) $N_2H_2\ell + \ell \rightleftharpoons NH\ell + NH\ell$
(7) $N\ell + H\ell \rightleftharpoons NH\ell + \ell$
(8) $NH\ell + H\ell \rightleftharpoons NH_2\ell + \ell$
(10) $NH_2\ell + H\ell \rightleftharpoons NH_3\ell + \ell$
(14) $NH_3\ell \rightleftharpoons NH_3 + \ell$

Mechanism 6
[8, 25]
(1) $H_2 + \ell \rightleftharpoons H_2\ell$
(2) $H_2\ell + \ell \rightleftharpoons H\ell + H\ell$
(3) $N_2 + \ell \rightleftharpoons N_2\ell$
(5) $N_2\ell + H_2\ell \rightleftharpoons N_2H_2\ell + \ell$
(6) $N_2H_2\ell + \ell \rightleftharpoons NH\ell + NH\ell$
(8) $NH\ell + H\ell \rightleftharpoons NH_2\ell + \ell$
(10) $NH_2\ell + H\ell \rightleftharpoons NH_3\ell + \ell$
(14) $NH_3\ell \rightleftharpoons NH_3 + \ell$

*Table 3* Summary of Computational Results and the Corresponding Computational Requirements

1. Independent pathways

| | Problem #1 | Problem #2 |
|---|---|---|
| Number of elementary reactions | 11 | 14 |
| Number of LPs | 13 | 581 |
| Computation time* | 0.06 s | 1.1 s |
| Number of combinatorially independent pathways | 6 | 35 |

2. Acyclic pathways (independent and combined)

| | Problem #1 | Problem #2 |
|---|---|---|
| Number of elementary reactions | 11 | 14 |
| Number of LPs | 35 | 984 |
| Computation time* | 0.06 s | 1.7 s |
| Number of combinatorially independent pathways | 17 | 367 |

*Pentium II Celeron 450 MHz PC, 128 MB RAM

## Result and Discussion

When applied to the set of 11 elementary reactions in *Table 1* [1-9, 25], the current method has recovered 6 independent mechanisms in 0.06 s on a PC (Pentium II Celeron 450 MHz and 128 MB RAM). All 6 mechanisms are identical with those available in the literature [1, 2, 7, 8, 25], which are listed as mechanisms 1 through 6 in *Table 2*. Moreover, the method has generated 17 acyclic combined mechanisms in 0.6 seconds on the same PC, 11 of which have resulted from linearly combining the 6 independent mechanisms. One of the combined mechanisms corresponds to the mechanism consisting of the 11 candidate elementary reactions [8]. It is worth noting that the number of elementary reactions reported in the literature is 9 instead of 11. This increase is a result of splitting the initiation step into 2 and adding the desorption step for $NH_3$ signifying termination. It is logical to postulate that the initiation proceeds in two steps, each involving a single active site and that the termination occurs through the desorption of $NH_3$ formed on the active site: Any elementary reaction would be far more likely to be bi-molecular than tri-molecular [7, 9, 13, 52, 53].

An extensive review of the available literature [4-6, 9] indicates that elementary reactions (11), (12), and (13), also listed in *Table 1*, are highly plausible to be in the pathway of ammonia-synthesis reaction. With the addition of these 3 elementary reactions, the current method has yielded 35 independent mechanisms in 1.1 seconds and 367 acyclic mechanisms in 1.7 seconds on the same PC, 332 of which have resulted from linearly combining the independent mechanisms. *Table 3* summarizes the results described above. Note that there is no direct correspondence between the computational effort required for the identification of independent feasible pathways and that required for the identification of acyclic feasible pathways. When the number of candidate elementary reactions is appreciable, the former tends to be greater than the latter: The two efforts resort to different sets of algorithms.

With the number of elementary balances remaining invariant at 2, one for nitrogen and the other for hydrogen, each increment in the number of elementary reactions automatically translates into an exponential magnification of combinatorial complexity, thereby adding substantially to the computational time for mechanism determination. It has been amply demonstrated that the current method is capable of coping with this added burden. Nevertheless, caution should be exercised so that an excessively large number of candidate elementary reactions is not proposed in implementing the current method; otherwise, we would be confronted with a bewildering number of feasible mechanisms, thus rendering inordinately difficult the final selection of the valid mechanism through experimental reaction–rate and spectroscopic measurements in conjunction with theoretical and computational studies. In fact, it is highly desirable that the final selection be conducted sequentially and iteratively starting with a relatively modest set of candidate elementary reactions which are plausible on the basis of empirical and theoretical evidence.

## Concluding Remarks

The current work has yielded a substantial number of stoichiometrically exact independent as well as acyclic combined candidiate mechanisms for deriving the rate law of the catalytic synthesis of ammonia. These mechanisms include those published hitherto, thereby validating them. Moreover, the current work has unequivocally demonstrated that the mathematically exact, graph-theoretic method presented herein for identifying such mechanisms is inordinately effective.

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## APPENDIX 1. FORMAL GRAPH-THEORETIC DESCRIPTION OF THE REACTION-PATHWAY-IDENTIFICATION PROBLEM

Here, a formal description is given of the problem of reaction-pathway identification. It is couched in the parlance of graph theory in general and that of P-graph in particular [34, 35, 39].

### Problem Definition

Let a reaction-pathway-identification problem be defined by triplet $(E, O, M)$, where $E$ is the overall reaction; $O = \{e_1, e_2, \ldots, e_n\}$, the finite ordered set of elementary reactions; $M = \{a_1, a_2, \ldots, a_l\}$, the finite ordered set of chemical and active species; $E = [E_1, E_2, \ldots, E_l]^T \in \mathbf{Z}^l$, where $E_j$ is the difference between the number of moles of the $j$-th chemical produced and that consumed by the overall reaction; and $e_i = [e_{1,i}, e_{2,i}, \ldots, e_{l,i}]^T \in \mathbf{Z}^l$, where $e_{j,i}$ is the difference between the number of moles the $j$-th chemical or active specie produced and that consumed by the $i$-th elementary-reaction step. Since every elementary reaction is reversible, both its forward and reverse steps are included in set $O$, i.e.,

$$\forall e_i \, (e_i \in O \Rightarrow -e_i \in O)$$

In other words, for any elementary-reaction step $e_i$ defined, its opposite step, denoted by $-e_i$, is also defined in the problem. It is assumed that

$$M \cap O = \varnothing \text{ and } E \notin O \cup M \, .$$

### Representation

Elementary reactions, chemicals, and active species are represented by P-graphs as follows:

For the overall reaction, $E$, let $\omega^-(E)$ and $\omega^+(E)$ denote the set of starting reactants (precursors) and final products (targets), respectively; it follows that

$$\omega^-(E) = \{a_j : a_j \in M, E_j < 0\}$$

and

$$\omega^+(E) = \{a_j : a_j \in M, E_j > 0\}.$$

If $\omega(E)$ is the set of chemical species consumed or produced by the overall reaction, $E$, we have naturally

$$\omega(E) = \omega^-(E) \cup \omega^+(E).$$

For any elementary-reaction step $e_i \in O$, let $\omega^-(e_i)$ and $\omega^+(e_i)$ denote the set of reactants and products of $e_i$, respectively; it follows that

$$\omega^-(e_i) = \{a_j : a_j \in M, e_{j,i} < 0\}$$

and

$$\omega^+(e_i) = \{a_j : a_j \in M, e_{j,i} > 0\}.$$

If $\omega(e_i)$ denotes the set of chemical and active species consumed or produced by the elementary-reaction step $e_i$, we have

$$\omega(e_i) = \omega^-(e_i) \cup \omega^+(e_i).$$

For any chemical or active species $a_j \in M$, let $\upsilon^-(a_j)$ and $\upsilon^-(a_j)$ denote the set of elementary-reaction steps consuming and producing $a_j$, respectively; it follows that

$$\upsilon^-(a_j) = \{e_i : e_i \in O, a_j \in \omega^+(e_i)\}$$

and

$$\upsilon^+(a_j) = \{e_i : e_i \in O, a_j \in \omega^-(e_i)\}.$$

If $\upsilon(a_j)$ denotes the set of elementary-reaction steps consuming or producing $a_j$, we have obviously

$$\upsilon(a_j) = \upsilon^-(a_j) \cup \upsilon^-(a_j).$$

For any set of the elementary-reaction steps, $o \subseteq O$, let $\Psi^-(o)$ and $\Psi^+(o)$ denote the set of chemical and active species consumed and produced by any element of $o$, respectively; it follows that

$$\Psi^-(o) = \bigcup_{e_i \in o} \omega^-(e_i)$$

and

$$\Psi^+(o) = \bigcup_{e_i \in o} \omega^+(e_i).$$

If $\Psi(o)$ is the set of chemical and active species consumed or produced by any element of $o$, we have

$$\Psi(o) = \Psi^-(o) \cup \Psi^+(o).$$

For any set of chemical or active species $m \subseteq M$, let $\varphi^-(m)$ and $\varphi^+(m)$ denote the set of elementary-reaction steps producing and consuming any element of $m$, respectively; it follows that

$$\varphi^-(m) = \bigcup_{a_j \in m} \upsilon^-(a_j)$$

and

$$\varphi^+(m) = \bigcup_{a_j \in m} \upsilon^+(a_j).$$

If $\varphi(m)$ is the set of elementary-reaction steps producing or consuming any element of $m$, we have

$$\varphi(m) = \varphi^{-}(m) \cup \varphi^{+}(m).$$

For any set of elementary-reaction steps $o \subseteq O$, let $\mathrm{X}(o)$ denote the set of opposite steps of the elementary-reaction steps included in set $o$; then,

$$\mathrm{X}(o) = \{e_i : -e_i \in \mathrm{o}\}.$$

Any P-graph representing a set of chemical or active species and elementary-reaction steps is given by pair $(m, o)$, where $o \subseteq O$ is the set of the elementary-reaction steps, and $m \subseteq M$ is the set of chemical and active species, where

$$\Psi(o) \subseteq m.$$

The set of vertices of the graph is

$$V = o \cup m,$$

where any vertex corresponding to set $m$ is termed M-type, and any vertex corresponding to set $o$ is termed O-type. The set of arcs is

$$A = A_1 \cup A_2,$$

where

$$A_1 = \{(a_j, e_i) : a_j \in m, e_i \in o, a_j \in \omega^{-}(e_i)\}$$

and

$$A_2 = \{(e_i, a_j) : e_i \in o, a_j \in m, a_j \in \omega^{+}(e_i)\}.$$

In graphical representation, vertices of the O-type are denoted by horizontal bars, and vertices of the M-type are denoted by solid circles.