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CHEMICAL MATROIDS. I.

Independence and Dependence in Chemical Reaction Systems

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(Abstract) An introductory summary of matroid theory that describes chemical interpretations of abstract structure of a given set is presented, where the set is made up of molecular species, reaction equations, reaction intermediates, or state variables in chemically reacting systems; thus algebraic relationships occurring in the systems are examined, which are associated with the general notion of independence/dependence of the set, and which are far apart from the physico-chemical properties of the chemical substances in the systems. The Nernst chain reaction mechanism as an example is analyzed by means of the theory.

I. Introduction

The concept of independence often plays an important role in the field of chemistry. Several words concerning it can

easily be found in a textbook[1] of chemical thermodynamics; for example, independent (thermodynamic) state variables, independent (chemical) reactions, independent constituents, and the degree of freedom in the phase. Horiuti and Nakamura[2] have pointed out that in steady states the number of independent reaction-pathways is equal to the subtraction of the number of independent reaction-intermediates from the number of elementary reactions. It has been shown[3] that chemically reacting systems in which every coupled reaction reaches equilibrium can be expressed as algebraic groups with finite rank (= the maximum number of independent reactions). The examples above-mentioned suggest that the algebraic properties of chemical systems, as distinct from the physico-chemical characters of individual substances, should be widely investigated. The present note is devoted to an introductory study of the properties of independence/dependence that can be found in chemical reaction theory.

The abstract properties of linear dependence for a given finite mathematical set have been studied by Whitney[4], who first named such a structure a matroid ("matrix" and "oid"). Following his definition of matroidal structure, we will develop the theory of chemical matroids. This mathematical theory will enable us to essentially understand the nature of independence/dependence in chemical fields.

II. Definition of Matroids

Let E be a finite set of distict elements, and let 2^E be the family of all subsets of E; $2^E = \{ X \mid X \subseteq E \}$. This set 2^E contains the empty set $\emptyset$. The number of elements in a subset

X is denoted by $|X|$, and that of 2^E by $2^{|E|}$. Assume that any X of 2^E can be determined whether it is dependent or independent; methods suitable for the determination are characterized by the nature of the elements of E.

If a nonempty subset F_I ($\subseteq 2^E$) fulfills the following postulates, called the independence axioms, then we can say that E has matroidal structure (or exactly saying, the pair of E and F_I is a matroid on E) :

(i-1) The empty set is independent: that is to say, $\emptyset \in F_I$.

(i-2) Any subset of an independent set is independent; that is, if $X \subseteq Y$ and $Y \in F_I$, then $X \in F_I$.

(i-3) If there are two independent sets X and Y such that $|Y| = |X| + 1$, then $X \cup \{y\}$ for $y \in Y - X$ is independent; namely, if $X, Y \in F_I$ and $|Y| > |X|$, then there is an element y in $Y - X$ for $X \cup \{y\} \in F_I$.

By use of the definition that a base is a maximum independent set, it can be derived[4] from the axioms (i-1,2, 3) that the set of bases, F_B, satisfies the following base axioms:

(b-1) The empty set $\emptyset$ is not a base; $\emptyset \notin F_B$.

(b-2) No proper subset of a base is a base; $X \subset Y$, $Y \in F_B \Rightarrow X \notin F_B$.

(b-3) If X and Y are bases and if x is an element of X, then there exists an element y in Y such that $(X - \{x\}) \cup \{y\}$ is a base; $X, Y \in F_B$, $x \in X \Rightarrow \exists y \in Y$: $(X - \{x\}) \cup \{y\} \in F_B$.

Inversely on the basis of the definition that a subset of E

is independent if it is contained in a base, the axioms of (i-1, 2, 3) can be obtained from the set (b-1, 2, 3); in other words, the two axiom sets are equivalent. This equivalence situation is valid for every pair of the postulate sets including the rank postulates and the circuit postulates in the following; if one of them is adopted as the postulate of matroids, then the others can be considered to be theorems.

The rank of a subset X, denoted by rk(X), is the maximum number of independent elements of X. The definition of matroids in terms of rank is thus given by:[6]

(r-1) $0 \leqq rk(X) \leqq |X|$ for $X \subseteq E$.

(r-2) If $X \subseteq Y$ ($\subseteq E$), then $rk(X) \leqq rk(Y)$.

(r-3) $rk(X \cup Y) + rk(X \cap Y) \leqq rk(X) + rk(Y)$ for $X, Y \subseteq E$.

A minimum dependent set $C \in F_D$ is called a circuit, where F_D is used to designate the family of dependent sets or all subsets of E not included in F_I. It becomes clear that circuits ($\in F_C$) fulfill the following axioms because no independent set contains circuits:[6]

(c-1) $\emptyset \notin F_C$.

(c-2) $X \subset Y$, $Y \in F_C \Longrightarrow X \notin F_C$.

(c-3) $X, Y \in F_C$, $x \in X \cap Y$, $y \in Y - X \Longrightarrow Z \in F_C : y \in Z \subseteq X \cup Y - \{x\}$.

III. Chemical Matroids

(molecular matroids) We consider a set of n_M molecular species in a chemically reacting system: $E_M = \{ M(1) \quad M(2) \quad \ldots \quad M(n_M) \}$. Let us assume that a subset X_M of E_M is independent

if no reaction-equation (stoichiometric) can be made up of elements of the subset, and dependent otherwise. By means of the matrix language it is easily shown that the stoichiometric independence with respect to chemical elements satisfies the postulates (i-1, 2, 3); when X_M is represented by a matrix $\underline{\underline{X}}_M$ whose columns are the composition matrices of the molecular species with respect to the chemical elements, the dependence means that there is a solution $\underline{q}_j$ for the matrix equation $\underline{\underline{X}}_M \underline{q}_j = 0$, where the column matrix $\underline{q}_j$ contains at least one nonzero integer. We will call E_M (or the pair of E_M and $F_I(E_M)$) a molecular matroid.

Example 1. The molecular species in the Nernst chain reaction mechanism

$$\text{"Cl} + H_2 \longrightarrow HCl + H\text{"} = q_{(1)}$$

$$\text{"H} + Cl_2 \longrightarrow HCl + Cl\text{"} = q_{(2)}$$

are set as E_M : $E_M = \{ H_2 \quad Cl_2 \quad HCl \quad H \quad Cl \}$, and its matrix representation

$$\underline{\underline{E}}_M = \begin{array}{c} \begin{matrix} H_2 & Cl_2 & HCl & H & Cl \end{matrix} \\ \begin{pmatrix} 2 & 0 & 1 & 1 & 0 \\ 0 & 2 & 1 & 0 & 1 \end{pmatrix} \end{array} \begin{matrix} \\ H \\ Cl \end{matrix}$$

We obtain the following.

$F_I(E_M) - F_B(E_M)$: $\emptyset$, $\{ H_2 \}$, $\{ Cl_2 \}$, $\{ HCl \}$, $\{ H \}$, $\{ Cl \}$.

$F_B(E_M)$: $\{ H_2 \quad Cl_2 \}$, $\{ H_2 \quad HCl \}$, $\{ H_2 \quad Cl \}$, $\{ Cl_2 \quad HCl \}$, $\{ Cl_2 \quad H \}$, $\{ HCl \quad H \}$, $\{ HCl \quad Cl \}$, $\{ H \quad Cl \}$.

$F_C(E_M)$: $\{ H_2 \quad H \}$, $\{ Cl_2 \quad Cl \}$, $\{ H_2 \quad Cl_2 \quad HCl \}$, $\{ H_2 \quad HCl \quad Cl \}$, $\{ Cl_2 \quad HCl \quad H \}$, $\{ HCl \quad H \quad Cl \}$.

$F_D(E_M)$ - $F_C(E_M)$: $\{H_2\ Cl_2\ H\}$, $\{H_2\ Cl_2\ Cl\}$, $\{H_2\ HCl\ H\}$, $\{H_2\ H\ Cl\}$, $\{Cl_2\ HCl\ Cl\}$, $\{Cl_2\ H\ Cl\}$, $\{H_2\ Cl_2\ HCl\ H\}$, $\{H_2\ Cl_2\ HCl\ Cl\}$, $\{H_2\ Cl_2\ H\ Cl\}$, $\{H_2\ HCl\ H\ Cl\}$, $\{Cl_2\ HCl\ H\ Cl\}$, $\{H_2\ Cl_2\ HCl\ H\ Cl\}$.

Note: $|E_M\} = n_M = 5$, $2^5 = 32$, $rk(E_M) = 2$.

(reaction matroids) Let a set of reaction equations q_1, ..., q_{n_Q} be given: $E_Q = \{q_1 \ldots q_{n_Q}\}$. We can say that a subset X_Q ($\subseteq E_Q$) is independent if there is no linear relation $\underline{X}_Q\underline{p}_j = 0$ ($\underline{p}_j \neq 0$, a column matrix with nonzero integers) , and dependent otherwise; this definition (stoichiometric independence with respect to molecular species) clearly fulfills the postulates (i-1, 2, 3), and corresponds to Jouguet's criterion[5] that is used commonly by chemists. The following example will show that $\underline{p}_j$ can be considered to be reaction pathways (or routes). E_Q is referred to below as a reaction matroid.

Example 2. The equations $q_{(1)}$, $q_{(2)}$, and q_{ov} = "$H_2 + Cl_2 \longrightarrow 2\ HCl$" (overall reaction) in the Nernst mechanism are chosen as the members of E_Q : $E_Q = \{q_{(1)}\ q_{(2)}\ q_{ov}\}$. Then the circuit of E_Q is E_Q only; that is, $q_{ov} = q_{(1)} + q_{(2)}$.

$$\underline{E}_Q = \begin{matrix} q_{(1)} & q_{(2)} & q_{ov} \end{matrix} \begin{pmatrix} -1 & 0 & -1 \\ 0 & -1 & -1 \\ 1 & 1 & 2 \\ 1 & -1 & 0 \\ -1 & 1 & 0 \end{pmatrix} \begin{matrix} H_2 \\ Cl_2 \\ HCl \\ H \\ Cl \end{matrix}, \quad \underline{p}_j = \begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix}$$

Example 3. The six circuits in Example 1 can be interpreted as reaction equations; then we use them as the elements of E_Q:

$E_Q = \{ q_1 \ldots q_6 \}$, where

$q_1 =$ "$H_2 \longrightarrow 2H$", $q_2 =$ "$Cl_2 \longrightarrow 2Cl$",

$q_3 =$ "$H_2 + Cl_2 \longrightarrow 2HCl$" $= q_{ov}$ (overall reaction),

$q_4 =$ "$H_2 + 2Cl \longrightarrow 2HCl$", $q_5 =$ "$Cl_2 + 2H \longrightarrow 2HCl$",

$q_6 =$ "$Cl + H \longrightarrow HCl$", and its matrix representation

$$\underline{E}_Q = \begin{array}{c} \begin{matrix} q_1 & q_2 & q_3 & q_4 & q_5 & q_6 \end{matrix} \\ \left(\begin{matrix} -1 & 0 & -1 & -1 & 0 & 0 \\ 0 & -1 & -1 & 0 & -1 & 0 \\ 0 & 0 & 2 & 2 & 2 & 1 \\ 2 & 0 & 0 & 0 & -2 & -1 \\ 0 & 2 & 0 & -2 & 0 & -1 \end{matrix} \right) \end{array} \begin{matrix} H_2 \\ Cl_2 \\ HCl \\ H \\ Cl \end{matrix}$$

$F_B(E_Q)$: $\{q_1\ q_2\ q_3\}$, $\{q_1\ q_2\ q_4\}$, $\{q_1\ q_2\ q_5\}$,
$\{q_1\ q_2\ q_6\}$, $\{q_1\ q_3\ q_4\}$, $\{q_1\ q_3\ q_6\}$,
$\{q_1\ q_4\ q_5\}$, $\{q_1\ q_5\ q_6\}$, $\{q_2\ q_3\ q_5\}$,
$\{q_2\ q_3\ q_6\}$, $\{q_2\ q_4\ q_5\}$, $\{q_2\ q_4\ q_6\}$,
$\{q_3\ q_4\ q_5\}$, $\{q_3\ q_4\ q_6\}$, $\{q_3\ q_5\ q_6\}$,
$\{q_4\ q_5\ q_6\}$.

$F_C(E_Q)$: $\{q_1\ q_3\ q_5\}$, $\{q_1\ q_4\ q_6\}$, $\{q_2\ q_3\ q_4\}$,
$\{q_2\ q_5\ q_6\}$, $\{q_1\ q_2\ q_3\ q_6\}$, $\{q_1\ q_2\ q_4\ q_5\}$,
$\{q_3\ q_4\ q_5\ q_6\}$.

Note: $rk(E_Q) = 3$, $q_2 + q_4 = q_3$, $q_1 + q_5 = q_3$, $q_1 + q_2 + 2q_6 = q_3$, $q_4 = q_1 + 2q_6$, $q_5 = q_2 + 2q_6$, $q_1 + q_2 + q_4 = q_5$, $q_3 + q_4 = q_5 + q_6$.

(reaction-intermediate matroids) Molecular species such as ions and free radicals, which are produced but not accumulated in chemically reacting systems under consideration, are called reaction intermediates. We assume that X_Q ($\subseteq F_Q$) is a set of elementary reactions that gives an overall reaction equation q_{ov} in a steady state: in other words, the matrix equation $\underline{X}_Q\underline{p}_j = \underline{q}_{ov}$ (a reaction pathway $\underline{p}_j \neq 0$) is given. $\underline{X}_Q$ and $\underline{q}_{ov}$ can be decomposed into composite matrices as

$$\underline{X}_Q = \left(\begin{array}{c} \underline{X}_{QM} \\ \hline \underline{X}_{QI} \end{array}\right) \quad \text{and} \quad \underline{q}_{ov} = \left(\begin{array}{c} \underline{q}_{ovM} \\ \hline \underline{q}_{ovI} \end{array}\right)$$

where the subscript M is concerned only with the molecular species in q_{ov}, and I with the intermediates. Note: $\underline{X}_{QI}$ is an $n_I \times |X_Q|$ matrix, where n_I is the number of intermediates. The matrix equation then leads to $\underline{X}_{QI}\underline{p}_j = \underline{q}_{ovI} = 0$ because the reaction intermediates of X_Q must vanish in the overall reaction. The definition of independence/dependence for a set of intermediates is thus established, and identical with that of Horiuti and Nakamura[2]. The number of independent reaction-intermediates is equal to the number of independent column matrices in the transpose of $\underline{X}_{QI}$, or to the number of independent linear forms of q_j's with constant coefficients $\underline{p}_j$.

Example 4. For the Nernst mechanism (Example 2), $\underline{X}_{QI}\underline{p}_j = 0$, where

$$\underline{X}_{QI} = \begin{array}{c} \begin{array}{cc} q_{(1)} & q_{(2)} \end{array} \\ \left(\begin{array}{cc} 1 & -1 \\ -1 & 1 \end{array}\right) \end{array} \begin{array}{l} \text{H} \\ \text{Cl} \end{array}, \quad \underline{p}_j = \left(\begin{array}{c} 1 \\ 1 \end{array}\right)$$

Only one of the intermediates is independent.

Example 5. Any circuit containing q_3 (= q_{ov}) in $F_C(E_Q)$ of Example 3 represents a reaction pathway for q_{ov}. Then in $\{q_1 \quad q_2 \quad q_3 \quad q_6\}$, for example, two reaction-intermediates are independent because of two linear relations

$$\begin{array}{c} \\ H \\ Cl \end{array} \begin{array}{c} \begin{array}{ccc} q_1 & q_2 & q_6 \end{array} \\ \begin{pmatrix} 2 & 0 & -1 \\ 0 & 2 & -1 \end{pmatrix} \end{array} \begin{pmatrix} 1 \\ 1 \\ 2 \end{pmatrix} = 0$$

(thermodynamic matroids) Let E_T be a set of thermodynamic state-variables of a gas of 1 mole: $E_T = \{ p \quad V \quad T \}$, (pressure, volume, temperature). Clearly, E_T becomes a matroid after the thermodynamic consideration of independence/dependence ($rk(E_T) = 2$); this is an example of non-matric matroids. Only one circuit is given by $\{ p \quad V \quad T \}$, which suggests the equation of states (e.g., $pV = RT$).

Let $E_T = \{ p \quad T \quad \xi \}$ be a set of chemical thermodynamic variables for a chemically reacting system (ξ, the extent of reaction); this also becomes a non-matric matroid with respect to chemical thermodynamic independence. Note that the set $\{ p \quad V \quad T \quad \xi \}$ is not a matroid because the postulate (i-3) fails.

(chemical dual matroids) We denote a dual matroid of E by E*. E and E* are duals if and only if there is a one-to-one correspondence between their elements such that bases in one set correspond to base complements in the other:[4] $F_B^* = \{ E - B \mid B \in F_B \}$. The dual of the independent family F_I is defined by $F_I^* = \{ E - X \mid B \subseteq X, B \in F_B \}$.

Example 6. For Example 1, F_B^* : $\{ HCl \quad H \quad Cl \}$, $\{ Cl_2 \quad H \quad Cl \}$, $\{ Cl_2 \quad HCl \quad H \}$, $\{ H_2 \quad H \quad Cl \}$, $\{ H_2 \quad HCl \quad Cl \}$, $\{ H_2 \quad Cl_2 \quad Cl \}$, $\{ H_2 \quad Cl_2 \quad H \}$, $\{ H_2 \quad Cl_2 \quad HCl \}$.

The elements of F_I^* (i.e., the independent sets of the dual matroid) are given by all of the subsets of the above bases.

Note: Every matroid has a dual.

IV. Properties of Chemical Matroids

Referring to some of the abstract theorems of Whitney's paper, we make a summary of chemical interpretations of properties of matroids, which is very useful in a study of independence/dependence in chemical fields.

1. The definition of nullity of X ($\subseteq$ E) is given by nl(X) = |X| - rk(X); for any X, nl(X) $\geq$ 0; if X $\subset$ Y , then nl(X) $\leq$ nl(Y); rk(E*) = nl(E), nl(E*) = rk(E). X is independent, or the elements of X are independent,if nl(X) = 0; otherwise X and its set of elements are dependent. In terms of these statements we can clearly define the concept of independence/dependence of the elements of X in chemical fields; for example, independent molecules, independent reaction-equations, independent reaction-intermediates. The number of

independent elements of X is equal to rk(X). Note: Any subset of a matroid is a matroid.

2. y is dependent on X if rk(X $\cup$ { y }) = rk(X); otherwise y is independent of X. By this method we can check whether an element of a chemical matroid is dependent on or independent of a subset of the matroid.

3. The rank of a matroid equals that of a base; rk(E) = rk(B). X is a base in E if and only if rk(X) = rk(E) and nl(X) = 0; if X and Y are bases, then $|X| = |Y|$. By means of these statements we can count the maximum number of independent elements of a chemical matroid in question. In the case of thermodynamic matroids, the maximum number corresponds to the degree of freedom (See 5. below). Note: A base is a maximum set containing no circuit; X is independent if and only if it is contained in a base.

4. As Examples 2 and 3 show, it is of great importance in chemical theory to study the properties of dependent sets, especially of circuits. Dependent sets of E_M are obviously interpreted as stoichiometric reaction equations in chemistry; for example, the dependent set { H_2 Cl_2 H } in Example 1 can be rewritten as $H_2 + Cl_2 \longrightarrow 2H + Cl_2$. The circuits of E_Q containing an overall reaction can be considered to be minimum reaction pathways. (See Example 2.) Note: The term "reaction pathway (or route)" is used by chemists as a set of chemical reaction steps that gives an overall reaction in question.

We obtain $\underset{\sim}{X}_M \underset{\sim}{q}_j = 0$ ($\underset{\sim}{q}_j \neq 0$) and $\underset{\sim}{X}_Q \underset{\sim}{p}_k = 0$ ($\underset{\sim}{p}_k \neq 0$) if X_M and X_Q are dependent sets. The first equation means the

conservation of chemical elements in the reaction equation q_j, and the second the conservation of molecular species in the reaction pathway p_k.

5. We directly obtain $rk(E^*) = |E| - rk(E)$ from the definition of the dual matroid E^* of E. This equation can be interpreted as: For a molecular matroid, $n_M - rk(E_M)$ is equal to the maximum number of independent reaction-equations. For a reaction matroid, $n_Q - rk(E_Q)$ equals the maximum number of independent reaction-pathways. The number of independent pathways for steady states is given by the subtraction of the number of independent reaction-intermediates from the number of elementary reactions, i.e., by $|X_Q| - rk(X_{QI}{}^t)$, (t, transpose). The last has been found by Horiuti and Nakamura,[2] who got it from the matrix algebraic point of view.

Chemical thermodynamics texts (e.g., Ref. 1) often describe the following relation; c - r' = the number of independent constituents, where c = the number of constituents, and r' = the number of reactions in a chemical thermodynamic system; this is just the equation above-mentioned.

6. E is said to be separable, if it is possible to divide the elements of E into two groups, $E_{(1)}$ and $E_{(2)}$, each containing at least one element, such that $rk(E) = rk(E_{(1)}) + rk(E_{(2)})$.[4] Separability in other words means that the groups have no interaction between them, and therefore each group can be dealt with separately. We hereafter consider chemical matroids to be non-separable.

If a dependent subset X_M (or X_Q) is separable, then it contains molecular species (or reaction equations) having no

relation to the reaction (or the pathway) of the set; for example, the set $\{ H_2 \quad Cl_2 \quad H \}$ in Example 1 is separable and is decomposed as $H_2 \longrightarrow 2H$ and $Cl_2 \longrightarrow Cl_2$ without interaction of the chemical elements. (The union of a set X and an element y is separable if y is independent of X.)
Note: Circuits are non-separable.

7. There exists only one circuit C, $x \in C \subseteq B \cup \{ x \}$, for $x \notin B \in F_B$; this circuit, called a fundamental circuit of x with respect to a base B, is denoted by $C(x \mid B) = \{ y \mid B \cup \{x\} - \{ y \} \in F_B \}$. The number of fundamental circuits of E for $x \in E - B$ is nl(E).

Example 7. For Example 3 we have

$C(q_4 \mid \{ q_1 \quad q_2 \quad q_3 \}) = \{ q_2 \quad q_3 \quad q_4 \}$,
$C(q_5 \mid \{ q_1 \quad q_2 \quad q_3 \}) = \{ q_1 \quad q_3 \quad q_5 \}$,
$C(q_6 \mid \{ q_1 \quad q_2 \quad q_3 \}) = \{ q_1 \quad q_2 \quad q_3 \quad q_6 \}$,
$C(q_3 \mid \{ q_4 \quad q_5 \quad q_6 \}) = \{ q_3 \quad q_4 \quad q_5 \quad q_6 \}$, etc.

If an element y is added to a base, then in the set there is necessarily a dependent set. Note: For a circuit C, $nl(C) > 0$, while, $X \subsetneq C$ implies $nl(X) = 0$; $|C| - 1 \leq |B|$ because the subtraction of one element from a circuit yields an independent set.

V. Simple Applications

(solution of indeterminate problems in stoichiometry) Let us consider the following reaction equations:

$$2KClO_3 \longrightarrow KCl + 2O + KClO_4 ,$$
$$3KClO_3 \longrightarrow 2KCl + 5O + KClO_4 ,$$
$$4KClO_3 \longrightarrow 2KCl + 4O + 2KClO_4 , \text{ etc.}$$

Each equation that satisfies stoichiometry involves the same kind of reactants and products as in the others; in other words, the stoichiometric coefficients of the molecular species are indeterminable. Such examples are known as indeterminate problems by chemists. This situation easily becomes understandable when the circuits are made up of the chemical species. (Recall that circuits can be uniquely determined.) In this example we set $E_M = \{ KClO_3 \quad KCl \quad O \quad KClO_4 \}$, and obtain the set of the circuits of E_M, $E_Q = \{ q_1 \cdot \cdot \cdot q_4 \}$, where q_1 = "$KClO_3 \longrightarrow KCl + 3O$", q_2 = "$4KClO_3 \longrightarrow 3KClO_4 + KCl$", q_3 = "$KClO_3 + O \longrightarrow KClO_4$", q_4 = "$KCl + 4O \longrightarrow KClO_4$". Any stoichiometric equation in the example is thus expressed as $n\, q_j + m\, q_k$ (n, m, integers; q_j and q_k $(j \neq k)$ are bases for E_Q) because $rk(E_Q) = 2$.

(Analysis of the Nernst chain reaction) All of the non-separable dependent sets of Example 1, of which the number is at most 11, is set as elements of E_Q : $E_Q = \{ q_1 \cdot \cdot \cdot q_{11} \}$. The first six elements $q_1, \ldots, q_6$ are the same as in Example 3. The other q_j's are indeterminable, and are written below, for instance, as:

$$q_7 = "2H_2 + Cl_2 \longrightarrow 2HCl + 2H",$$
$$q_8 = "H_2 + 2Cl_2 \longrightarrow 2HCl + 2Cl",$$

q_9 = "H_2 + Cl $\longrightarrow$ HCl + H" = $q_{(1)}$,

q_{10} = "Cl_2 + H $\longrightarrow$ HCl + Cl" = $q_{(2)}$,

q_{11} = "H_2 + Cl_2 $\longrightarrow$ HCl + H+Cl".

Note: $rk(E_Q) = 3$, $rk(E_Q^*) = 8$, $q_7 = q_1 + q_3$, $q_8 = q_2 + q_3$, $2q_9 = q_1 - q_2 + q_3$, $2q_{10} = -q_1 + q_2 + q_3$, $2q_{11} = q_1 + q_2 + q_3$.

The reaction pathways (or the nonseparable dependent sets of E_Q) containing q_3 (= q_{ov}) in linear form are given by $q_3 = q_1 + q_5$, $q_3 = q_9 + q_{10}$, . . ., $q_3 = q_1 + q_2 + 2q_6$, . . . , in which the second form is just the Nernst mechanism.

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