

## 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<sup>1</sup> 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<sup>2</sup> 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<sup>3</sup> 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<sup>4</sup>, 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 distinct 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<sup>4</sup> 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:<sup>6</sup>

$$(r-1) \quad 0 \leq rk(X) \leq |X| \quad \text{for } X \subseteq E.$$

$$(r-2) \quad \text{If } X \subseteq Y (\subseteq E), \text{ then } rk(X) \leq rk(Y).$$

$$(r-3) \quad rk(X \cup Y) + rk(X \cap Y) \leq rk(X) + rk(Y) \text{ for } X, Y \subseteq E.$$

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:<sup>6</sup>

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

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

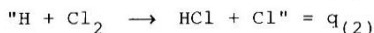
$$(c-3) \quad X, Y \in F_C, x \in X \cap Y, y \in Y - X \implies Z \in F_C : y \in Z \subseteq X \cup Y - \{x\}.$$

### III. Chemical Matroids

(molecular matroids) We consider a set of  $n_M$  molecular species in a chemically reacting system:  $F_M = \{ M(1) M(2) \dots M(n_M) \}$ . Let us assume that a subset  $X_M$  of  $F_M$  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  $\underline{X}_M$  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  $\underline{X}_M \underline{q}_j = 0$ , 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



are set as  $E_M : E_M = \{ \text{H}_2 \quad \text{Cl}_2 \quad \text{HCl} \quad \text{H} \quad \text{Cl} \}$ , and its matrix representation

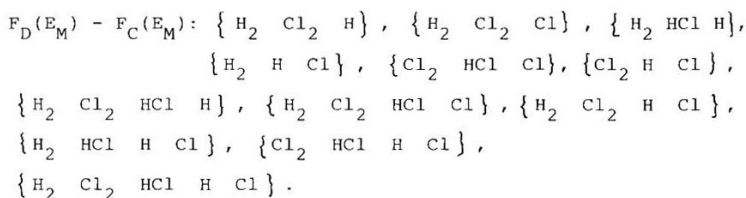
$$E_M = \begin{matrix} & \text{H}_2 & \text{Cl}_2 & \text{HCl} & \text{H} & \text{Cl} \\ \begin{pmatrix} 2 & 0 & 1 & 1 & 0 \\ 0 & 2 & 1 & 0 & 1 \end{pmatrix} & & & & \text{H} & \\ & & & & & \text{Cl} \end{matrix}$$

We obtain the following.

$$F_I(E_M) - F_B(E_M): \emptyset, \{ \text{H}_2 \}, \{ \text{Cl}_2 \}, \{ \text{HCl} \}, \{ \text{H} \}, \{ \text{Cl} \}.$$

$$F_B(E_M): \{ \text{H}_2 \quad \text{Cl}_2 \}, \{ \text{H}_2 \quad \text{HCl} \}, \{ \text{H}_2 \quad \text{Cl} \}, \{ \text{Cl}_2 \quad \text{HCl} \}, \\ \{ \text{Cl}_2 \quad \text{H} \}, \{ \text{HCl} \quad \text{H} \}, \{ \text{HCl} \quad \text{Cl} \}, \{ \text{H} \quad \text{Cl} \}.$$

$$F_C(E_M): \{ \text{H}_2 \quad \text{H} \}, \{ \text{Cl}_2 \quad \text{Cl} \}, \{ \text{H}_2 \quad \text{Cl}_2 \quad \text{HCl} \}, \{ \text{H}_2 \quad \text{HCl} \quad \text{Cl} \}, \\ \{ \text{Cl}_2 \quad \text{HCl} \quad \text{H} \}, \{ \text{HCl} \quad \text{H} \quad \text{Cl} \}.$$



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

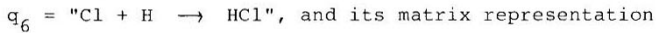
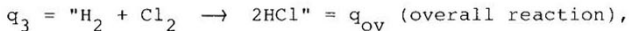
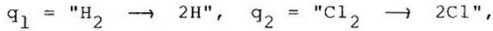
(reaction matroids) Let a set of reaction equations  $q_1, \dots, q_{n_Q}$  be given:  $E_Q = \{q_1 \dots q_{n_Q}\}$ . We can say that a subset  $X_Q$  ( $\subseteq E_Q$ ) is independent if there is no linear relation  $\sum_{Q \in X_Q} p_j = 0$  ( $p_j \neq 0$ , a column matrix with nonzero integers), 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<sup>5</sup> 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  $q_{ov} = "H_2 + Cl_2 \rightarrow 2 HCl"$  (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,  $q_{ov} = q_{(1)} + q_{(2)}$ .

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

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

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



$$E_Q = \begin{array}{cccccc} & q_1 & q_2 & q_3 & q_4 & q_5 & q_6 & \\ \left( \begin{array}{cccccc} -1 & 0 & -1 & -1 & 0 & 0 \\ 0 & -1 & -1 & 0 & -1 & 0 \\ 0 & 0 & 2 & 2 & 2 & 1 \\ 2 & 0 & 0 & 0 & -2 & -1 \\ 0 & 2 & 0 & -2 & 0 & -1 \end{array} \right) & \begin{array}{l} \text{H}_2 \\ \text{Cl}_2 \\ \text{HCl} \\ \text{H} \\ \text{Cl} \end{array} \end{array}$$

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

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

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

(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  $X_Q p_j = q_{ov}$  (a reaction pathway  $p_j \neq 0$ ) is given.  $X_Q$  and  $q_{ov}$  can be decomposed into composite matrices as

$$X_Q = \begin{pmatrix} X_{QM} \\ X_{QI} \end{pmatrix} \quad \text{and} \quad q_{ov} = \begin{pmatrix} q_{ovM} \\ q_{ovI} \end{pmatrix}$$

where the subscript M is concerned only with the molecular species in  $q_{ov}$ , and I with the intermediates. Note:  $X_{QI}$  is an  $n_I \times |X_Q|$  matrix, where  $n_I$  is the number of intermediates. The matrix equation then leads to  $X_{QI} p_j = q_{ovI} = 0$  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<sup>2</sup>. The number of independent reaction-intermediates is equal to the number of independent column matrices in the transpose of  $X_{QI}$ , or to the number of independent linear forms of  $p_j$ 's with constant coefficients  $p_j$ .

Example 4. For the Nernst mechanism (Example 2),  $X_{QI} p_j = 0$ ,

where

$$X_{QI} = \begin{matrix} & q_{(1)} & q_{(2)} \\ \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} & H & , & p_j = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ & c_1 & & \end{matrix}$$



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  $\{q_1, q_2, q_3, q_6\}$ , for example, two reaction-intermediates are independent because of two linear relations

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

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

Let  $E_T = \{p, T, \xi\}$  be a set of chemical thermodynamic variables for a chemically reacting system ( $\xi$ , the extent of reaction); this also becomes a non-matric matroid with respect to chemical thermodynamic independence. Note that the set  $\{p, V, T, \xi\}$  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:<sup>4</sup>  $F_B^* = \{ E - B \mid B \in F_B \}$ . 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,  $F_B^* : \{ \text{HCl H Cl} \}, \{ \text{Cl}_2 \text{ H Cl} \}, \{ \text{Cl}_2 \text{ HCl H} \}, \{ \text{H}_2 \text{ H Cl} \}, \{ \text{H}_2 \text{ HCl Cl} \}, \{ \text{H}_2 \text{ Cl}_2 \text{ Cl} \}, \{ \text{H}_2 \text{ Cl}_2 \text{ H} \}, \{ \text{H}_2 \text{ Cl}_2 \text{ HCl} \}$ .

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  $\text{rk}(X)$ . Note: Any subset of a matroid is a matroid.

2.  $y$  is dependent on  $X$  if  $\text{rk}(X \cup \{y\}) = \text{rk}(X)$ ; 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;  $\text{rk}(E) = \text{rk}(B)$ .  $X$  is a base in  $E$  if and only if  $\text{rk}(X) = \text{rk}(E)$  and  $\text{nl}(X) = 0$ ; 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  $H_2 + Cl_2 \rightarrow 2H + Cl_2$ . 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  $\sum_M q_j = 0$  ( $q_j \neq 0$ ) and  $\sum_Q p_k = 0$  ( $p_k \neq 0$ ) 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,<sup>2</sup> 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  $rk(E) = rk(E_{(1)}) + rk(E_{(2)})$ .<sup>4</sup> 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  $\{H_2, Cl_2, H\}$  in Example 1 is separable and is decomposed as  $H_2 \rightarrow 2H$  and  $Cl_2 \rightarrow Cl_2$  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  $C(x | B) = \{y | B \cup \{x\} - \{y\} \in F_B\}$ . The number of fundamental circuits of  $E$  for  $x \in E - B$  is  $nl(E)$ .

Example 7. For Example 3 we have

$$C(q_4 | \{q_1, q_2, q_3\}) = \{q_2, q_3, q_4\},$$

$$C(q_5 | \{q_1, q_2, q_3\}) = \{q_1, q_3, q_5\},$$

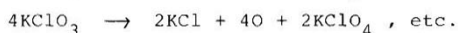
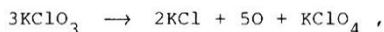
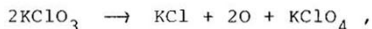
$$C(q_6 | \{q_1, q_2, q_3\}) = \{q_1, q_2, q_3, q_6\},$$

$$C(q_3 | \{q_4, q_5, q_6\}) = \{q_3, q_4, q_5, q_6\}, \text{ etc.}$$

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,  $x \notin C$  implies  $nl(x) = 0$ ;  $|C| - 1 \leq |B|$  because the subtraction of one element from a circuit yields an independent set.

#### V. Simple Applications

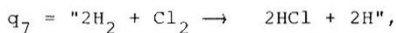
(solution of indeterminate problems in stoichiometry) Let us consider the following reaction equations:

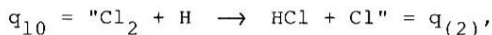
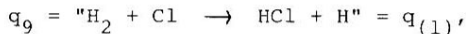


Each equation that satisfies stoichiometry involves the same kind of reactants and products as in the others; in other words, the stoichiometric coefficients of the molecular species are indeterminable. Such examples are known as indeterminate problems by chemists. This situation easily becomes understandable when the circuits are made up of the chemical species. (Recall that circuits can be uniquely determined.)

In this example we set  $E_M = \{ \text{KClO}_3 \quad \text{KCl} \quad \text{O} \quad \text{KClO}_4 \}$ , and obtain the set of the circuits of  $E_M$ ,  $E_Q = \{ q_1 \cdot \cdot \cdot q_4 \}$ , where  $q_1 = " \text{KClO}_3 \rightarrow \text{KCl} + 3\text{O} "$ ,  $q_2 = " 4\text{KClO}_3 \rightarrow 3\text{KClO}_4 + \text{KCl} "$ ,  $q_3 = " \text{KClO}_3 + \text{O} \rightarrow \text{KClO}_4 "$ ,  $q_4 = " \text{KCl} + 4\text{O} \rightarrow \text{KClO}_4 "$ . 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  $\text{rk}(E_Q) = 2$ .

(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  $q_1, \cdot \cdot \cdot, q_6$  are the same as in Example 3. The other  $q_j$ 's are indeterminable, and are written below, for instance, as:





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

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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