224. Note Concerning the Concepts of Reaction Numbers, Independent Reactions and Resistant Groups in Chemical Thermodynamics and Kinetics

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(23. V. 72)

Summary. A linear algebraic characterization for sets of independent reactions, independent reaction numbers, conservation laws and resistant groups for both equilibrium and kinetic systems is suggested. Basing on the ranks of two stochiometric matrices N and M, these concepts are discussed and formulas given for setting up of independent sets of equilibrium and kinetic equations. The difference in the definition of independent reaction numbers for these two types of systems is pointed out. A brief consideration is devoted to the transformations of equilibrium and kinetic equations induced by transformation from one set of linearly independent reactions to another. Finally the conservation laws are formulated as chemical invariants within the N, M framework.

1. Introduction. – In this note we wish to give an algebraic definition of concepts which play an important role in the stochiometry of thermodynamics and kinetics of complex systems of chemical reactions. The concept of independent reactions and resistant groups (components) is used as a standard procedure to formulate chemical equilibrium [1]. Algebraic formulations of these have been suggested by several authors, *cf. Lielmezs* [2], *Gavalas* [3] and by *Aris* [4].

Nevertheless, both are treated in an intuitive way, though they play a fundamental role in many fields of physical chemistry and therefore more concise definitions might be of practical value.

Since some time a linear algebraic technique for formulation of the stochiometry of complex chemical reaction systems for both equilibrium and kinetic systems has been used at our laboratory, which is based on the concept of reaction numbers introduced by *Schottky et al.* [5] [6], *De Donder* [7] and used by many authors in the field of chemical thermodynamics [8] [9]. Since this approach appears to offer a particularly systematic way for the formulation of the concepts mentioned above, we intend with this note to publish a set of formulae relating stochiometry, independent reactions, independent particle numbers and conservation laws for arbitrarily complicated chemical reaction systems. For both the case of equilibrium and kinetic systems a systematic way for deriving a sufficient set of equations of equilibrium state or motion will be given. Finally some remarks concerning symmetry groups of such systems are made. The following notations and assumptions will be used. For simplicity it is assumed that only one phase is considered in the system. However, extension to any number β of phases is straightforward and needs barely explicit formulation besides those given in the text. Similarly the presence of charged par-

ticles may be considered. Relevant particles present in the system will be denoted by A_i, i = 1, 2,..., A and any reaction $\mathcal{R}_j$ between these by

$$\mathcal{R}_j = \sum_{i=1}^{A} \nu_{ji} A_i = 0 \qquad j = 1, 2, ..., \bar{R}. \tag{1}$$

In multiphase systems one and the same particle present in β different phases may by considered as β distinguishable different species. Then the processes transfering the particle from one phase to another have to be included in the set of reactions occuring in the system.

A reaction number ξ_j to any reaction $\mathcal{R}_j$ is assigned, which relates mole numbers initially and actually present in the system by

$$n_i(\xi) = n_{io} + \sum_{j=1}^{\bar{R}} \xi_j \nu_{ji}, \, i = 1, 2, ..., A. \tag{2}$$

Under appropriate conditions, analogs of Eq. (2) may be written for molalities m_i and molarities c_i [10], i.e.

$$m_i = m_{io} + \sum_{j=1}^{\bar{R}} \xi_j(\nu_{ji}/m_0), \, i = 1, 2, ..., A \tag{2'}$$

$$c_i = c_{io} + \sum_{j=1}^{\bar{R}} \xi_j(\nu_{ji}/V), \, i = 1, 2, ..., A \tag{2''}$$

where

$$m_0 = 10^{-3} n_0 M_0, \, M_0 \text{ is the molar mass of the solvent in g mol}^{-1}.$$

Eq. (2') is exact if the solvent A_0 is inert under all reactions occuring in the system and applies in general approximately if $m_i \ll m_0$ for all i = 1, 2,..., A. Eq. (2'') applies for phases with constant volume V and is approximately applicable for condensed phases even at moderate concentrations.

The symbol $[A_i]$ will be used to denote the concentration of particle A_i, expressed either as molar fractions, molality or molarity. It is always understood that concentration measures are consistent with the standard states chosen for any phase (system) considered.

Every relevant particle A_i is stochiometrically defined by a formula unit

$$A_i = E^1_{\mu_i 1} E^2_{\mu_i 2} \dots E^E_{\mu_i E} \tag{3}$$

where $E^1 E^2 \dots E^E$ denotes the nuclides building up the set of particles $A_1, A_2, ..., A_A$ and the coefficients μ_i are the usual stochiometric coefficients. Depending on the situation, the different nuclides of an element may or may not be relevant and often only the elemental composition of each particle has to be taken into account.

The formalism will be restricted to ideal systems but is applicable to all real systems for which there exists a unique relation between activities and concentrations of all relevant particles.

2.1. Stochiometric matrix, reaction numbers, independent reactions and independent particle concentrations. – If an A dimensional particle space R^A is introduced, whose base vectors are assigned to the relevant particles A_i, i = 1, 2,.., A,

then any one of the reactions (1) may be considered as a vector of this space and the set of all reactions $\mathcal{R}_1, \ldots, \mathcal{R}_{\overline{R}}$ may be written as

$$N(A) = (0). \tag{4}$$

The jth row of the stochiometric matrix N is given by the stochiometric coefficients ν_{ji}, $i = 1, 2, \ldots, A$ according to Eq. (1), therefore N is an $\overline{R} \times A$ rectangular matrix. (A) and (0) denote a symbolic vector whose components are the particles and the zero vector, respectively, both of dimension $A \times 1$.

The form of Eq. (4) is conserved if appropriate definitions of the stochiometric matrix N are used for matrix formulation of Eqs. (2), (2'), (2''), viz.

$$\{\tilde{n}\} = \{\tilde{n}_0\} + \{\tilde{\xi}\}\, N \tag{5}$$

$$\{\tilde{m}\} = \{\tilde{m}_0\} + \{\tilde{\xi}\}\, N \tag{5'}$$

$$\{\tilde{c}\} = \{\tilde{c}_0\} + \{\tilde{\xi}\}\, N. \tag{5''}$$

In Eq. (5) $\{\tilde{n}\}$, $\{\tilde{m}\}$, and $\{\tilde{c}\}$ denote the row matrices $\{n_1, n_2, \ldots, n_A\}$ etc. of the mole numbers, molalities and molarities, respectively, with dimension $1 \times A$. $\{\tilde{\xi}\}$ stands for the $1 \times \overline{R}$ row matrix $\{\xi_1 \xi_2 \ldots \xi_{\overline{R}}\}$ of the reaction numbers.

Let $R \leqslant \min(\overline{R}, A)$ be the rank $R = r(N)$ of N. For the following we assume N ordered in a way such that the first r rows and columns are linearly independent. As a consequence N may be divided into sub-matrices according to

$$N = \begin{pmatrix} N^{R,R} & N^{R,A-R} \\ N^{\overline{R}-R,R} & N^{\overline{R}-R,A-R} \end{pmatrix} \tag{6}$$

where the upper indices denote row and column numbers of the subblocks and

$$|N^{R,R}| \neq 0.$$

Correspondingly the rows of mole numbers (molalities and molarities) and reaction numbers may be divided, i.e.

$$\{\tilde{n}\} = \{\tilde{n}^R\ \tilde{n}^{A-R}\} \tag{7}$$

hence

$$\{\tilde{n}^R\ \tilde{n}^{A-R}\} = \{\tilde{n}_0^R\ \tilde{n}_0^{A-R}\} + \{\tilde{\xi}^R \tilde{\xi}^{\overline{R}-R}\} \begin{pmatrix} N^{R,R} & N^{R,A-R} \\ N^{\overline{R}-R,R} & N^{\overline{R}-R,A-R} \end{pmatrix} \tag{8}$$

There exist two matrices $P(\overline{R}-R; R)$ and $Q(R, A-R)$, such that

$$P(N^{R,R}\ N^{R,A-R}) = (PN^{R,R}\ PN^{R,A-R}) = (N^{\overline{R}-R,R}\ N^{\overline{R}-R,A-R}) \tag{9}$$

$$\begin{pmatrix} N^{R,R} \\ N^{\overline{R}-R,R} \end{pmatrix} Q = \begin{pmatrix} N^{R,R}Q \\ N^{\overline{R}-R,R}Q \end{pmatrix} = \begin{pmatrix} N^{R,A-R} \\ N^{\overline{R}-R,A-R} \end{pmatrix} \tag{10}$$

with

$$P = N^{\overline{R}-R,R}(N^{R,R})^{-1} \tag{9'}$$

$$Q = (N^{R,R})^{-1}\, N^{R,A-R}. \tag{10'}$$

The matrices P and Q may be given a simple interpretation. The rows of P give the linear combinations of reactions $\mathcal{R}_1, \mathcal{R}_2, \ldots, \mathcal{R}_R$ by which the reactions $\mathcal{R}_{R+1}, \mathcal{R}_h, \mathcal{R}_{\overline{R}}$ are represented, viz.

$$\mathcal{R}_h = \sum_{j=1}^{R} P_{hj}\, \mathcal{R}_j, \, h = R+1, \ldots, \overline{R} \tag{11}$$

$$\nu_{hi} = \sum_{j=1}^{R} P_{hj}\, \nu_{ji}, \, i = 1, 2, \ldots, A. \tag{11'}$$

Therefore the reactions $\mathcal{R}_1, \ldots, \mathcal{R}_R$ may be considered as an independent set, by which all other reactions $\mathcal{R}_{R+1}, \ldots, \mathcal{R}_{\overline{R}}$ may be linearly expressed. Correspondingly the mass law constants of the latter may be expressed by

$$K_h = \prod_{j=1}^{R} K_j{}^{P_{hj}} = \prod_{j=1}^{R} \left(\prod_{i=1}^{A} [A_i]^{\nu_{ji}} \right)^{P_{hj}}$$

$$= \prod_{i=1}^{A} \prod_{j=1}^{R} [A_i]^{\nu_{ji}\, P_{hj}} = \prod_{i=1}^{A} [A_i]^{\sum_{j=1}^{R} P_{hj}\nu_{ji}} \tag{12}$$

$$= \prod_{i=1}^{A} [A_i]^{\nu_{hi}}, h = R+1, \ldots, \overline{R}.$$

The set of linearly independent reactions is not uniquely determined in general, since any subset of R linearly independent rows of N may be chosen as a representative. The interrelation among the different choices will be discussed in section 2.2.3.

2.2. Equilibrium state. – For equilibrium systems any admissible choice of any particular set of linearly independent reactions is sufficient for calculation of the equilibrium state of the phase (system) under consideration.

2.2.1. – If chemical potentials are used the equilibrium conditions may be written according to (4)
$$N(\mu_i) = (0).$$

This linear homogeneous system has a non-trivial solution if $R = r(N) < A$ [11].

Using the ordering of N as assumed above then

$$N^{R,R}(\mu^R) + N^{R,A-R}(\mu^{A-R}) = (0)$$
$$(\mu^R) = -N^{(R,R)-1}\, N^{R,A-R}(\mu^{A-R}). \tag{13}$$

Eq. (13) shows that A–R chemical potentials may be chosen arbitrarily, which then determine (μ^R) uniquely. Therefore A–R further equations have to be provided by conservation laws (see 2.2).

2.2.2. If equilibrium constants are used for determination of the equilibrium state, we first express concentrations $[A_i]$, $i = 1, 2, \ldots, A$ by the reaction numbers $\tilde{\xi}^R$ of a set of linearly independent reactions

$$\{n^R \, \tilde{n}^{A-R}\} = \{\tilde{n}_0^R \, \tilde{n}_0^{A-R}\} + \{\tilde{\xi}\} \, (N^{R,R} \, N^{R,A-R}) \tag{14}$$

and insert these into the Eq.

$$K_j = \prod_{i=1}^{A} [A_i]^{\nu_{ji}}, \, j = 1, 2, \ldots, R \tag{12'}$$

which provide R equations for determination of the equilibrium reaction number vector $\tilde{\xi}_{eq}^R$. No explicit recurrence to conservation laws has been made, since these are implicitly contained in Eq. (14). One therefore may consider the vectors $\tilde{\xi}^R$ and $\tilde{n}^R$ as a vector of independent reaction numbers and a vector of independent mole numbers (concentrations) of equilibrium systems.

Comparing the two approaches 2.2.1 and 2.2.2 one may state that they have some analogy to nod and mesh analysis in linear network theory. Obviously the number of equations to be solved in the two approaches is $A-R$ and $R = r$ (N), respectively. Therefore it may be advantageous to use 2.2.1 if $A-R < R$ and 2.2.2 if $R < A-R$.

2.2.3. Transformations of the equilibrium equations induced by different choices of sets of independent reactions. – As mentioned in section 2.1 the choice of a set of independent reactions is in general not unique. Once such a set $\tilde{R} = \{R_1, \ldots, R_R\}$ has been chosen, any other admissible set $\tilde{\bar{R}} = \{\bar{R}_1, \bar{R}_2 \ldots \bar{R}_R\}$ is expressible as a transformation induced by a linear operator $\hat{T}$, viz.

$$\hat{T}\{R\} = \{\bar{R}\} = T\{R\} \tag{15}$$

where T is a nonsingular rational matrix. Written in components

$$\bar{R}_j = \sum_{\bar{j}=1}^{R} T_{j\bar{j}} R_{\bar{j}} = \sum_{i=1}^{A} \bar{\nu}_{ji} A_i; \; j = 1, 2, \ldots, R \tag{16}$$

hence

$$\bar{\nu}_{ji} = \sum_{\bar{j}=1}^{R} T_{j\bar{j}} \nu_{\bar{j}i}, \; j = 1, 2, \ldots, R, \; i = 1, 2, \ldots, A \tag{17}$$

$$(\bar{N}^{R,R} \; \bar{N}^{R,A-R}) = T(N^{R,R}, N^{R,A-R}) = (TN^{R,R}, TN^{R,A-R}). \tag{18}$$

Furthermore, $\hat{T}$ induces a linear transformation of the vector $\tilde{\xi}^R$ of independent reaction numbers, since we require that any chemical state of the system must be uniquely expressible by any choice of a linearly independent set

$$\{\tilde{n}^R \; \tilde{n}^{A-R}\} = \{\tilde{n}_0^R \; \tilde{n}_0^{A-R}\} + \tilde{\xi}^R(N^{R,R} \; N^{R,A-R})$$

$$= \{\tilde{n}_0^R \; \tilde{n}_0^{A-R}\} + \tilde{\bar{\xi}}^R(\bar{N}^{R,R} \; \bar{N}^{R,A-R}), \tag{19}$$

$$\tilde{\bar{\xi}}^R \, T = \tilde{\xi}^R.$$

Eq. (15) and (20) show that the vectors of independent reactions and independent reaction numbers transform contragrediently, i.e.

$$\tilde{\xi}R = \tilde{\bar{\xi}}\bar{R} \tag{20}$$

under the group of rational matrices T of degree R. The equilibrium equations $K_j = \varPi[A_i]^{\nu_{ji}}, \; j = 1, 2, \ldots, R$ transform uniquely into

$$\overline{K}_j(\tilde{\xi}) = \prod_{i=1}^{A} \lceil A_i\rfloor^{\overline{\nu}_{ji}} = \prod_{i=1}^{A} \lceil A_i\rfloor^{\sum\limits_{\overline{j}=1}^{R} T_{j\overline{j}}\nu_{\overline{j}i}}$$

$$= \prod_{i=1}^{A} \prod_{\overline{j}=1}^{R} \lceil A_i\rfloor^{T_{j\overline{j}}\nu_{\overline{j}i}} = \prod_{\overline{j}=1}^{R} \prod_{i=1}^{A} \lceil A_i\rfloor^{T_{j\overline{j}}\nu_{\overline{j}i}} = \qquad (21)$$

$$= \prod_{\overline{j}=1}^{R} \left(\prod_{\overline{j}=1}^{R} \lceil A_i\rfloor^{\nu_{\overline{j}i}} \right)^{T_{j\overline{j}}},$$

$$= \prod_{\overline{j}=1}^{R} K_{\overline{j}}(\xi)^{T_{j\overline{j}}},$$

which corresponds to Eq. (16) and expresses the fact that the logarithms of the equilibrium constants of sets of independent reactions transform cogrediently to the sets of independent reactions, i.e.

$$\hat{T}(\ln K) = (\ln \overline{K}) = T(\ln K). \qquad (22)$$

In general the $(\overline{R}-R, R)$ matrix P introduced by Eq. (9) is related to a particular matrix T, more exactly to some rows of it.

As a symmetry group of an equilibrium system one may define the set of non-singular rational linear transformations $\tilde{\overline{\xi}} = \tilde{\xi} \cdot T^{-1}$, which leave the set of equilibrium equations invariant. At the present time very little seems to be known about such groups, besides the trivial case of permutations and monomial transformations.

However, it should be mentioned that transformations of the type $\overline{N}^{R, R} = TN^{R, R}$ might be useful to find sets of independent reactions to which sets of equations for the equilibrium vector $\tilde{\xi}_{eq}$ of lowest degree belong. According to Eqs. (17), (18) and (22) this is equivalent to find matrices $\overline{N}^{R, R}$, $\overline{N}^{R, A-R}$ with as many coefficients of lowest possible modulus (maximally simplified system of equilibrium equations). As to our knowledge this aspect of complex chemical equilibrium systems has not yet been systematically investigated, though it might be of practical importance.

3. Kinetic systems. – 3.1. *Introductory remarks and notation.* – In contrast to equilibrium systems there may occur more than $R = r(N)$ reactions in kinetic systems which are kinetically relevant. As a matter of experience, it however is improbable that kinetically relevant reactions have higher molecularity and order than two, i.e. for most of the kinetically relevant reactions at most four of the stochiometric coefficients ν_{ji} are non zero, and their moduli $|\nu_{ji}| \leqslant 2$.

For the following we shall assume that the set $\mathcal{R}_1, \mathcal{R}_2, \ldots, \mathcal{R}_{\overline{R}}$ of reactions with stochiometric matrix N comprises all kinetically relevant reactions between the kinetically relevant particles $A_1, A_2, \ldots, A_A$ of the phase (system). Again N is supposed to be ordered in a way that the first $R = r(N) \leqslant \overline{R}$ rows of N are linearly independent (see sect. 2.1). The rate equations are assumed to be given by expressions of the type

$$\dot{\xi}_j = \frac{d\xi_j}{dt} = f_j([A], \pi), j = 1, 2 \ldots, \overline{R} \qquad (23)$$

where [A] denotes the concentration vector and π symbolizes all relevant physical state parameters of the system. Furthermore, it is assumed that linear relations

connect concentrations $[A_i]$ with reaction numbers either exactly or approximately, viz.

$$\{[\tilde{A}]^R[\tilde{A}]^{A-R}\} = \{[\tilde{A}]_0^R[\tilde{A}]_0^{A-R}\}$$

$$+ \{\tilde{\xi}^R\,\tilde{\xi}^{\bar{R}-R}\} \begin{pmatrix} N^{R,\,R} & N^{R,\,A-R} \\ N^{\bar{R}-R,\,R} & N^{\bar{R}-R,\,A-R} \end{pmatrix},$$

$$\{[\tilde{A}]\} = \tilde{\xi}N. \tag{24}$$

Basing on these assumptions, systems of independent kinetic equations (i.e. equations of motion) may be obtained either in terms of concentrations or in terms of independent reaction numbers. The latter concept should, however, be modified in the case of kinetic systems. This may be elucidated as follows. According to Eqs. (8), (9), (10) the particle concentration equations may be written as

$$[\tilde{A}]^R = [\tilde{A}]_0^R + \tilde{\xi}^R N^{R,\,R} + \tilde{\xi}^{\bar{R}-R} P N^{R,\,R} = [\tilde{A}]_0^R + (\tilde{\xi}^R + \tilde{\xi}^{\bar{R}-R}P)N^{R,\,R} \tag{25}$$

$$[\tilde{A}]^{A-R} = [\tilde{A}]_0^{A-R} + \tilde{\xi}^R N^{R,\,A-R} + \tilde{\xi}^{\bar{R}-R}N^{\bar{R}-R,\,A-R}$$

$$= [\tilde{A}]_0^{A-R} + \tilde{\xi}^R N^{R,\,A-R} + \tilde{\xi}^{\bar{R}-R}P N^{R,\,A-R}$$

$$= [A]_0^{A-R} + (\tilde{\xi}^{\bar{R}} + \tilde{\xi}^{R-R}P)\, N^{R,\,A-R} \tag{26}$$

(17) and (18) show that the vector $\tilde{\xi}^R + \tilde{\xi}^{\bar{R}-R}P$ represents the set of independent reaction numbers for kinetic systems, in contrast to equilibrium systems, for which the vector $\tilde{\xi}^R$ plays this role. It therefore seems appropriate to introduce the notation

$$\tilde{X}^R = \tilde{\xi}^R + \tilde{\xi}^{\bar{R}-R}P \tag{27}$$

for the vector of kinetic independent reaction numbers. Therefore

$$([\tilde{A}]^R - [\tilde{A}]_0^R)\,(N^{R,\,R})^{-1} = \tilde{X}^R \tag{25'}$$

$$[\tilde{A}]^{A-R} - [\tilde{A}]_0^{A-R} = \tilde{X}^R N^{R,\,A-R} = ([\tilde{A}]^R - [\tilde{A}]_0^R)\,(N^{R,\,R})^{-1}N^{R,\,A-R}. \tag{26'}$$

According to (25') and (26') one may appropriately denote $([A]^R)$ as vector of independent concentrations. Obviously Eq. (25') is the kinetic analog of (14).

3.2. *Systems of independent kinetic equations.* – From Eqs. (15), (17) and (18) systems of independent kinetic equations either in terms of independent concentrations or independent reaction numbers may be obtained as follows

$$\tilde{X}^R = \tilde{\xi}^R + \tilde{\xi}^{R-R}P = [\overset{\cdot}{\tilde{A}}]^R(N^{R,\,R})^{-1}$$

$$= \tilde{f}^R([A]^R, [\tilde{A}]^{A-R}, \pi) + \tilde{f}^{R-R}([\tilde{A}]^R, [\tilde{A}]^{A-R}, \pi)\cdot P$$

$$= \tilde{f}^R([\tilde{A}]^R, [\tilde{A}]_0^{A-R} + ([\tilde{A}]^R - [\tilde{A}]_0^R)\,(N^{R,\,R})^{-1}N^{R,\,A-R}, \pi)$$

$$+ \tilde{f}^{\bar{R}-R}([\tilde{A}]^R, [\tilde{A}]_0^{A-R} + ([\tilde{A}]^R - [\tilde{A}]_0^R)\,(N^{R,\,R})^{-1}N^{R,\,A-R}, \pi)P$$

$$= \tilde{f}^R([\tilde{A}]_0^R + \tilde{X}^R N^{R,\,R}, [\tilde{A}]_0^{A-R} + \tilde{X}^R N^{R,\,A-R}, \pi)$$

$$+ \tilde{f}^{\bar{R}-R}([\tilde{A}]_0^R + \tilde{X}^R N^{R,\,R}, [A]_0^{A-R} + \tilde{X}^R N^{R,\,A-R}, \pi)\, P. \tag{28}$$

From this set of equations either a system of equations of motion for the vector (X^R) of independent reaction numbers or for the vector $(|A]^R)$ of independent particle concentrations may be selected (irreducible systems of equations of motion).

3.2.1. As a special case we consider a kinetic system of R independent reactions $\mathcal{R}_1, \mathcal{R}_2, \ldots, \mathcal{R}_R$ with reaction numbers $\tilde{\xi}^R = \{\xi_1 \xi_2 \ldots \xi_R\}$ and their back reactions $-\mathcal{R}_1, -\mathcal{R}_2, \ldots, -\mathcal{R}_R$ with reaction numbers $\tilde{\xi}_-^R = \{\xi_{-1} \xi_{-2} \ldots \xi_{-R}\}$. As a consequence $\tilde{X}^R = \tilde{\xi}^R - \tilde{\xi}_-^R = \{\xi_j - \tilde{\xi}_{-j}\} = \{\tilde{X}_j\}$, i.e. the components of the independent reaction number vectors are the differences of the reaction numbers of each forward-backward reaction pair. In this case the equilibrium state is given by

$$\tilde{\dot{X}}^R = \tilde{O} = \tilde{f}^R(X_{eq}^R) - \tilde{f}_-^R(\tilde{X}_{eq}^R) \tag{29}$$

which determines the equilibrium value $\tilde{X}_{eq}^R$ of the reaction number vector. The relation of $\tilde{X}_{eq}^R$ to $\tilde{\xi}_{eq}^R$ may be obtained from Eqs. (14) and (25)

$$[\tilde{A}]_{eq}^R = [\tilde{A}]_0^R + \tilde{\xi}_{eq}^R N^{R,R} = [\tilde{A}]_0^R + \tilde{X}_{eq}^R N^{R,R} \tag{30'}$$

hence

$$\tilde{X}_{eq}^R = \tilde{\xi}_{eq}^R \tag{30''}$$

provided the initial conditions are chosen appropriately for both descriptions.

If not all of the back reactions are kinetically relevant, one obtains for any pair forward-backward reaction a component $X = \xi - \xi_-$ of the vector $\tilde{X}^R$ of independent reaction numbers.

3.2.2 Kinetic systems with pseudo-equilibrium steps may be treated by including a set of independent equilibrium equations $K_j = \prod_i (A_i)^{\nu_{ji}}$ into the set of equations of motion. Since either a reaction is kinetically relevant or a pseudo-equilibrium step, the latter play the role of conditions to the set of independent equations of motion and should be treated as such.

3.3. Transformations of kinetic equations induced by transformation in the space of linearly independent reactions may be formulated in complete analogy to section 2.2.3. If $\hat{T}$ is a linear operator according to Eqs. (15), then, according to (11) and (17)

$$\hat{T} \begin{pmatrix} \mathcal{R}_{R+1} \\ \vdots \\ \mathcal{R}_{\bar{R}} \end{pmatrix} = \hat{T} \, P \begin{pmatrix} \mathcal{R}_1 \\ \vdots \\ \mathcal{R}_R \end{pmatrix} = PT \begin{pmatrix} \mathcal{R}_1 \\ \vdots \\ \mathcal{R}_R \end{pmatrix} = \begin{pmatrix} \mathcal{R}_{R+1} \\ \vdots \\ \bar{\mathcal{R}}_{\bar{R}} \end{pmatrix}$$

with

$$\nu_{hi} = \sum_{j=1}^R P_{hj} \sum_{\bar{j}=1}^R T_{j\bar{j}} \, \nu_{\bar{j}i} = \sum_{\bar{j}=1}^R \left(\sum_{j=1}^R P_{hj} T_{j\bar{j}} \right) \nu_{\bar{j}i}$$

i.e.

$$(N^{\bar{R}-R,\,R} \;\; N^{\bar{R}-R,\,A-R}) = PTN^{R,\,R} \;\; PTN^{R,\,A-R}) \tag{31}$$

and therefore by (26) and (27)

$$\tilde{X}^R T = \tilde{X} \tag{32}$$

Eq. (32) is the analog of Eq. (19) and may be used to transform the system of kinetic equations (28) from one set of independent equations to any other admissible set.

The remarks made in sect. 2.2.4 concerning symmetry groups and maximally simplified systems of equations also apply to kinetic systems in strictly the same sense.

4. Conservation laws and resistent groups. – For every chemical system the number of nuclei of each nuclide present in the system is a chemical invariant. The conservation laws may therefore be expressed conveniently by means of the (A, E) matrix $M = (\mu_{ik})$, which relates the particle vector (A) to the vector (E) of nuclides present in the system. As specified in section 1, Eq. (3) may then be written

$$(A) = M(E) \tag{33}$$

Hence from (4)

$$NM = (0) \tag{34}$$

and the conservation of the vector of numbers of nuclides is directly given from

$$\{\tilde{n}_E\} = \{\tilde{n}^R \, \tilde{n}^{A-R}\} \, M$$

$$= [\{\tilde{n}_0^R \, \tilde{n}_0^{A-R}\} + \tilde{\xi}^R(N^{R,R} \, N^{R,A-R})] \, M$$

$$= \{\tilde{n}_0^R \, \tilde{n}_0^{A-R}\} \, M = \{\tilde{n}_0\} \, M. \tag{35}$$

Symbolically the conservation laws may be expressed by the linear form

$$\{\tilde{n}_E\} \, (E)$$

in which each term characterized by a nuclide is a chemical invariant.

The vector of initial mole numbers is a non-negative, otherwise arbitrary vector and M is a non-negative matrix of rank

$$r(M) = \mu \leqslant \min(A, E) \tag{36'}$$

where the ranks R, μ of N and M, respectively, are interrelated [12] by

$$R + \mu \leqslant A. \tag{36''}$$

Therefore the number of independent conservation laws may now be shown to equal μ. Without reordering the stochiometric matrix N the vector of nuclides (elements) may be ordered in a way that the first μ columns of M are linearly independent, i.e. the (A, E) matrix M is ordered as a divided matrix $M = (M^\mu \, M^{E-\mu})$. M^μ is a (A, μ) submatrix of M with rank $\mu = r(M) = r(M^\mu \leqslant \min (A, E)$ and $M^{E-\mu}$ is a (A, E-μ) matrix. Hence there exists a uniquely defined (μ, A) matrix 0, such that

$$M^\mu 0 = M^{E-\mu}, \text{ where } M = (M^\mu \, M^\mu 0). \tag{37}$$

Consequently the conservation law reads

$$\{\tilde{n}_E\} = \{\tilde{n}_0\} \, (M^\mu \, M^\mu 0) = \{\tilde{n}_0 M^\mu \, \tilde{n}_0 M^\mu 0) \tag{38}$$

$$= \{\tilde{n}_E{}^\mu \, \tilde{n}_E^\mu 0\} = \{\tilde{n}_E^\mu, \, \tilde{n}_E^{E-\mu}\}.$$

Obviously only the first μ nuclide numbers n_{E1}, n_{E2}, ..., $n_{E\mu}$ are independent invariants, whereas $n_{E\mu+1}$, $n_{E\mu+2}$, ..., n_{EE} are linearly dependent on the former ones. One therefore may introduce symbolic aggregates

$$F^1, F^2, , F^\mu$$

which may be called resistant groups and

$$F^\varkappa = E^1_{\mu_{\varkappa 1}} E^2_{\mu_{\varkappa 2}} \cdot \cdot E^\mu_{\mu_{\varkappa \mu}}, \varkappa = 1, 2, ..., \mu \tag{39}$$

may be defined by μ linearly independent rows of M^μ building up a rational non-singular (μ, μ) submatrix $M^{\mu,\mu}$ of M^μ

$$(F^\mu) = \begin{pmatrix} F^1 \\ F^2 \\ \vdots \\ F^\mu \end{pmatrix} = M^{\mu,\mu} \begin{pmatrix} E^1 \\ E^2 \\ \vdots \\ E^\mu \end{pmatrix} = M^{\mu,\mu}(E^\mu), |M^{\mu,\mu}| \neq 0. \tag{40}$$

Consequently the linearly independent conservation laws of the number of nuclides $E^1, E^2, ..., E^\mu$ may be written symbolically

$$\{\tilde{n}^\mu_E\} (E^\mu) = \{\tilde{n}^\mu_E\} (M^{\mu,\mu})^{-1}(F^\mu) = \{\tilde{n}^\mu_F\} (F^\mu)$$

i.e. $$\{\tilde{n}^\mu_F\} M^{\mu,\mu} = \{\tilde{n}^\mu_E\}. \tag{41}$$

As in the case of linearly independent sets of reactions the choice of the set of resistant groups is not unique in general, since every non-singular (μ, μ)- submatrix of M leads to a set of μ resistant groups. Any such choices, however, are interrelated by rational non-singular transformations and therefore in a certain sense equivalent.

Eq. (34) implies that the rank of the product NM is zero. This is obviously the case already for the products

$$(N^{R,R} N^{R,A-R}) M \tag{43'}$$

$$(N^{R,R}, N^{R,A-R}) M^\mu. \tag{43''}$$

From an algebraic point of view any set of independent reactions may be interpreted as a complete solution of the equation

$$XM = (0).$$

However, we shall not discuss this aspect of the stochiometric matrix here further [13], [14].

BIBLIOGRAPHY

[1] *K. Denbigh*, The Principles of Chemical Equilibrium (Cambridge, The University Press, 1964), p. 167.

[2] *J. Lielmezs*, Chem. Eng. Sci. *20*, 363 (1965).

[3] *G. R. Gavalas*, Nonlinear Differential Equations of Chemically Reacting Systems (Springer Verlag, Berlin, 1968), p. 2; where further references are given.

[4] *R. Aris*, Chem. Eng. Sci. *18*, 554 (1963); Arch. Rational Mech. Anal. *19*, 81 (1965); *ibid. 27*, 356 (1968).

[5] *H. Ulich*, Chemische Thermodynamik (Verlag Steinkopff, Dresden, 1930).
[6] *W. Schottky, H. Ulich & C. Wagner*, Thermodynamik (Berlin 1929).
[7] *Th. De Donder*, L'Affinité (Paris 1931).
[8] *I. Prigogine & R. Defay*, Chemical Thermodynamics (Longmans, Green & Co., London 1954).
[9] *J. G. Kirkwood & I. Oppenheim*, Chemical Thermodynamics (McGraw Hill Book Comp., New York (1961), p. 103.
[10] Symbols and Definition, IUPAC Bulletin Information No. 52.
[11] *H. v. Mangoldt & K. Knopp*, Einführung in die höhere Mathematik (S. Hirzel, Leipzig 1942), Vol. 1, p. 93.
[12] *W. Gröbner*, Matrizenrechnung (R. Oldenburg, München 1956), p. 96.
[13] *C. C. MacDuffee*, The Theory of Matrices (Chelsea Publishing Company, New York 1946), p. 10.
[14] *W. Gröbner, loc. cit.*, p. 97.

Erratum

Helv. *55*, 1532 (1972), Abhandlung Nr. 150 von *H. Hauth* und *D. Stauffacher*: In der Nomenklatur der Verbindungen **20** bis **32** (p. 1541 bis 1544) muss es anstelle von -4α, 14-didemethyl- korrekterweise -4β, 14-didemethyl- heissen.

EUCHEM – Konferenz über Optische Aktivität

Caen (Frankreich), 7.–9. Mai 1973

«Biopolymere, Induzierte *Cotton*-Effekte (durch Lösungsmittel und Magnetfelder), Semi-empirische Regeln und Theorie».

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