7 Outline of Applications of CRS

In this section, we first expand on section 2.2 about the importance of CRS in chemical equililibrium (7.1) and kinetics (7.2). We then briefly note two aspects of CRS (not treated in this tutorial) for advanced study (7.3 and 7.4).

7.1 Applications in Chemical Equilibrium

7.1.1 Computation of chemical equilibrium

CRS may be used in the calculation of the chemical equilibrium composition of a system (for example, at fixed T and P) using a so-called *stoichiometric* formulation (Smith and Missen, 1982, 1991, Chapter 6). Such an algorithm employs a complete set of R linearly independent chemical equations representing the law of conservation of mass and charge for the system, and then solves the set of nonlinear equations:

$$\Delta G_j \equiv \sum_{i=1}^{N} \nu_{ij}\mu_i = 0; j = 1, 2, \ldots, R \tag{61}$$

where ΔG_j is the change in the Gibbs function for chemical equation j, and μ_i is the chemical potential of species i. Equation (61) can be rewritten in terms of equilibrium constants. If we set

$$\mu_i = \mu_i^0(T, P^0, X^0) + RT \ln a_i \tag{62}$$

where $\mu_i^0(T, P^0, X^0)$ (henceforth denoted by $\mu_i^0(T)$) is the *standard chemical potential* of species i at the system T, standard-state pressure P^0, and standard-state composition X^0, and a_i is the *activity* of species i, (61) may be written as

$$\Delta G_j^0 = -RT \ln K_{aj}; j = 1, 2, \ldots, R \tag{63}$$

where ΔG_j^0 is the standard change in the Gibbs function for chemical equation j and K_{aj} is the corresponding equilibrium constant:

$$\begin{aligned} \Delta G_j^0 &= \sum_{i=1}^{N} \nu_{ij}\mu_i^0(T) && (64) \\ K_{aj} &= \Pi_{i=1}^{N} a_i^{\nu_{ij}}; j = 1, 2, \ldots, R && (65) \end{aligned}$$

It is important to note that *any* proper set of chemical equations may be used in the stoichiometric formulation (however, especially for large systems, there are computational considerations in set selection; see Smith and Missen, 1982, 1991, section 6.4, for details).

7.1.2 Species data (μ_i^0) from equilibrium constant data ($\Delta G_j^0, K_{aj}$)

In addition to the stoichiometric formulation of the chemical equilibrium problem, there is a *nonstoichiometric* formulation, which minimizes the total system Gibbs function, G, subject to the mass- and charge-balance constraints, solving the problem:

$$\min\ G \equiv \sum_{i=1}^{N} n_i \mu_i \tag{66}$$

$$\text{such that} \quad \sum_{i=1}^{N} a_{ki} n_i = b_k; k = 1, 2, \ldots M \tag{67}$$

Algorithms using the nonstoichiometric formulation are often referred to as "free-energy minimization algorithms", although this term is misleading, since *any* chemical equilibrium algorithm can be viewed as solving a minimization problem (equations (61) are a set of necessary conditions satisfied at the minimum of G).

An algorithm of either type may be used for any given problem, provided that the appropriate data are available. For a stoichiometric algorithm, the required thermochemical data are the quantities ΔG_j^0 (or K_{aj}); for a nonstoichiometric algorithm, the corresponding data are the standard chemical potentials of each species, $\mu_i^0(T)$. For a large number of species, the latter quantities have been determined and are available in tabular form (*e.g.*, JANAF, 1985). However, for many systems (for example, many biochemical and geochemical systems), data are only available in the form of ΔG_j^0 or K_{aj}. An apparent conclusion (*e.g.*, Björnbom, 1975, 1978; Anderson and Crerar, 1993, pp.517-518; Nordstrom and Nunoz, 1994, p. 401) is that nonstoichiometric algorithms cannot be used in such cases. This conclusion is not valid; methods of linear algebra like those used in MRM can be used to calculate a set of $\mu_i^0(T)$ from a set of ΔG_j^0 or K_{aj} (Smith, 1976, 1978; Smith and Missen, 1982, 1991, section 9.4; Cheluget *et al.*, 1987).

The key to calculating a set of $\mu_i^0(T)$ from a set of ΔG_j^0 or K_{aj} is the realization that equations (64) can be considered to be a set of R linear equations in the N unknown quantities $\mu_i^0(T)$. Thus, *any* solution of these equations may be used in a nonstoichiometric (or even in a stoichiometric) algorithm. We say that such a set is *consistent with* the set of ΔG_j^0 or K_{aj}. We show how to carry out the procedure using a method based on MRM by means of a simple example (Smith and Missen, 1982, 1991, pp. 216-217).

Example 10:
For the system $\{(\mathrm{H_3PO_4}, \mathrm{H_2PO_4^-}, \mathrm{HPO_4^{2-}}, \mathrm{PO_3^{3-}}, \mathrm{H^+}, \mathrm{OH^-}, \mathrm{H_2O}), (\mathrm{H,O,P,p})\}$, suppose that data are given in the form

$$\begin{aligned}
\mathrm{H_3PO_4} &= \mathrm{H_2PO_4^-} + \mathrm{H^+};\ \mathrm{K_1} && (68)\\
\mathrm{H_2PO_4^-} &= \mathrm{HPO_4^{2-}} + \mathrm{H^+};\ \mathrm{K_2} && (69)\\
\mathrm{HPO_4^{2-}} &= \mathrm{PO_4^{3-}} + \mathrm{H^+};\ \mathrm{K_3} && (70)\\
\mathrm{H_2O} &= \mathrm{OH^-} + \mathrm{H^+};\ K_4 = K_w/a_{\mathrm{H_2O}} && (71)
\end{aligned}$$

where $\mathrm{K_1}$ to $\mathrm{K_4}$ are the equilibrium constants for the reactions as written, and K_w is the ion-product for water. To find a consistent $\{\mu_i^0\}$ for the seven species of the system, we first calculate $\Delta G_j^0 \equiv -RT \ln K_j$ and form the matrix

$$(\mathbf{N}^T, -\mathbf{\Delta G}^0) = \begin{array}{c} \begin{array}{cccccccc} (1) & (2) & (3) & (4) & (5) & (6) & (7) & \\ \end{array} \\ \left(\begin{array}{cccccccc} -1 & 1 & 0 & 0 & 1 & 0 & 0 & -\Delta G_1^0 \\ 0 & -1 & 1 & 0 & 1 & 0 & 0 & -\Delta G_2^0 \\ 0 & 0 & -1 & 1 & 1 & 0 & 0 & -\Delta G_3^0 \\ 0 & 0 & 0 & 0 & 1 & 1 & -1 & -\Delta G_4^0 \end{array}\right) \end{array}$$

The unit matrix form of this is

$$\begin{array}{c} \begin{array}{cccccccc} (1) & (2) & (3) & (6) & (5) & (4) & (7) & \\ \end{array} \\ \left(\begin{array}{cccccccl} 1 & 0 & 0 & 0 & -3 & -1 & 0 & \Delta G_1^0 + \Delta G_2^0 + \Delta G_4^0 \\ 0 & 1 & 0 & 0 & -2 & -1 & 0 & \Delta G_2^0 + \Delta G_3^0 \\ 0 & 0 & 1 & 0 & -1 & -1 & 0 & \Delta G_3^0 \\ 0 & 0 & 0 & 1 & 1 & 0 & -1 & -\Delta G_4^0 \end{array}\right) \end{array}$$

A consistent $\{\mu_i^0\}$ with the species ordered as specified is $\{\Delta G_1^0 + \Delta G_2^0 + \Delta G_3^0, \Delta G_2^0 + \Delta G_3^0, 0, 0, -\Delta G_4^0, 0\}$. If we write the R (=4) stoichiometric equations represented by the first N (=7) entries in each of the rows of the unit matrix form, we see that the method in effect sets standard chemical potentials for R noncomponent species (here $\mathrm{H_3PO_4}$, $\mathrm{H_2PO_4^-}$, $\mathrm{HPO_4^{2-}}$, and $\mathrm{OH^-}$)

relative to a set of C (=3) component species (here H^+, PO_4^{3-}, and H_2O), which are assigned zero values. This is analogous to the usual assignment of standard chemical potentials relative to the elements, the "ultimate" components.

7.2 Applications in Chemical Kinetics

7.2.1 Number of independent steps (F_s) in a reaction network

A *reaction network* or *kinetics scheme* is a representation of the sequence of events or of a reaction pathway in a reacting system. It takes the form of a set of chemical *reactions* involving only "observable" species (that is, excluding reactive intermediates, such as free radicals). The set of reactions may involve reversible steps, and steps in series and/or parallel. The maximum number of independent steps in a reaction network, F_s, is an experimentally determined quantity. F_s is the number of stoichiometric degrees of freedom of the system. From CRS, the maximum value of F_s is R. A role of the network is to enable calculation of the complete compositional state of the reaction system, say, as a function of time. The information is in the form of a rate law for each step (obtained experimentally), including values of the rate parameters, such as order of reaction and Arrhenius parameters.

To illustrate reaction networks, consider the important process for making ethylene (C_2H_4) by dehydrogenation of ethane (C_2H_6). The simplest reaction network for this is the single step

$$C_2H_6 \rightarrow C_2H_4 + H_2 \tag{72}$$

If methane (CH_4) is formed in addition in significant amount as an "observed" species, we can expand (72) as a two-step network:

$$\begin{aligned} C_2H_6 &\rightarrow C_2H_4 + H_2 && (73)\\ C_2H_6 + H_2 &\rightarrow 2CH_4 && (74) \end{aligned}$$

In either case of (72) or (73) and (74), we do not *necessarily* imply that reaction takes place in the manner indicated.

Reaction (72) corresponds to the single chemical equation ($R = 1$) that we obtain (*e.g.*, by MRM) for the system {(C_2H_6, H_2, C_2H_4), (C,H)}:

$$C_2H_6 = C_2H_4 + H_2 \tag{75}$$

The set of reactions (73) and (74) corresponds to the set of chemical equations ($R = 2$) that we obtain for the system $\{(C_2H_6, H_2, C_2H_4, CH_4), (C,H)\}$:

$$\begin{aligned} C_2H_6 &= C_2H_4 + H_2 && (76)\\ C_2H_6 + H_2 &= 2CH_4 && (77) \end{aligned}$$

7.2.2 Determination of F_s implied by a reaction mechanism using CRS

A *reaction mechanism* is a more detailed representation of the sequence of events or reaction pathway than is a reaction network. The set of chemical reactions in a mechanism, called *elementary steps*, involves not only "observable" species, but also transient species or reactive intermediates, whose concentrations remain very small. (The number of elementary steps in a reaction mechanism may be greater than the value of R corresponding to the complete species list including the transient species.) Each step is postulated to represent an actual encounter between molecular species so as to react to form other species. We may call the observable species *major species*, and the reactive intermediates, whether molecular species or molecular fragments such as free radicals, *minor species*.

A postulated reaction mechanism (Rice and Herzfeld, 1934) for ethane decomposition to ethylene involves the following five steps:

$$\begin{aligned} C_2H_6 &\rightarrow 2CH_3^\bullet && (78)\\ CH_3^\bullet + C_2H_6 &\rightarrow CH_4 + C_2H_5^\bullet && (79)\\ C_2H_5^\bullet &\rightarrow C_2H_4 + H^\bullet && (80)\\ H^\bullet + C_2H_6 &\rightarrow H_2 + C_2H_5^\bullet && (81)\\ H^\bullet + C_2H_5^\bullet &\rightarrow C_2H_6 && (82) \end{aligned}$$

where $CH_3^\bullet$, $C_2H_5^\bullet$ and $H^\bullet$ are free radicals (minor species); the reaction mechanism also involves CH_4, which may be considered to be either a minor species (case (a)) or a major species (case (b)).

We can use the techniques of CRS (*i.e.*, MRM) to construct the reactions of a network from those of the mechanism, and simultaneously to determine F_s. This is done by linearly combining the steps of the mechanism so as to eliminate the minor species, by means of the following procedure, analogous to that used in MRM:

1. Write the stoichiometric coefficients of the mechanism in a matrix $\mathbf{N}$, with the rows corresponding to the reaction steps and the columns corresponding to the species. Label the rows and columns of the matrix, and place the minor species in the *initial* columns of the matrix.
2. Use elementary row operations to produce a unit matrix as large as possible in the upper left hand corner of $\mathbf{N}$, resulting in a matrix $\mathbf{N}^*$.
3. The reactions of the network are contained in the bottom-most rows of $\mathbf{N}^*$, those that do not involve the minor species (there are zero entries for these species in those rows).
4. The value of F_s is given by the number of reactions of the resulting reaction network.

For the above mechanism, the steps are as follows:

1.

$$\mathbf{N} = \begin{array}{c|rrrrrrr} & \mathrm{CH_3^\bullet} & \mathrm{C_2H_5^\bullet} & \mathrm{H^\bullet} & \mathrm{CH_4} & \mathrm{C_2H_6} & \mathrm{H_2} & \mathrm{C_2H_4} \\ R_1 & 2 & 0 & 0 & 0 & -1 & 0 & 0 \\ R_2 & -1 & 1 & 0 & 1 & -1 & 0 & 0 \\ R_3 & 0 & -1 & 1 & 0 & 0 & 0 & -1 \\ R_4 & 0 & 1 & -1 & 0 & -1 & 1 & 0 \\ R_5 & 0 & -1 & -1 & 0 & 1 & 0 & 0 \end{array}$$

2.

$$\mathbf{N}^* = \begin{array}{c|rrrrrrr} & \mathrm{CH_3^\bullet} & \mathrm{C_2H_5^\bullet} & \mathrm{H^\bullet} & \mathrm{CH_4} & \mathrm{C_2H_6} & \mathrm{H_2} & \mathrm{C_2H_4} \\ R_1 & 1 & 0 & 0 & 0 & 0 & -1/2 & -1/2 \\ R_2 & 0 & 1 & 0 & 0 & 0 & -1/2 & -1 \\ R_3 & 0 & 0 & 1 & 0 & 0 & -1/2 & 0 \\ R_4 & 0 & 0 & 0 & 1 & 0 & -1 & -1/2 \\ R_5 & 0 & 0 & 0 & 0 & 1 & -1 & -1 \end{array}$$

3. The rows in $\mathbf{N}^*$ may be interpreted to provide the following five reactions, which are necessarily not elementary steps:

$$\mathrm{CH_3^\bullet} - 1/2\mathrm{H_2} - 1/2\mathrm{C_2H_4} \rightarrow 0; \quad \text{or} \quad \mathrm{CH_3^\bullet} \rightarrow 1/2\mathrm{H_2} + 1/2\mathrm{C_2H_4} \tag{83}$$

$$\mathrm{C_2H_5^\bullet} - 1/2\mathrm{H_2} - \mathrm{C_2H_4} \rightarrow 0; \quad \text{or} \quad \mathrm{C_2H_5^\bullet} \rightarrow 1/2\mathrm{H_2} + \mathrm{C_2H_4} \tag{84}$$

$$H^{\bullet} - 1/2H_2 \rightarrow 0; \quad \text{or} \quad H^{\bullet} \rightarrow 1/2H_2 \tag{85}$$

$$CH_4 - H_2 - 1/2CH_4 \rightarrow 0; \quad \text{or} \quad CH_4 \rightarrow H_2 + 1/2CH_4 \tag{86}$$

$$C_2H_6 - H_2 - C_2H_4 \rightarrow 0; \quad \text{or} \quad C_2H_6 \rightarrow H_2 + C_2H_4 \tag{87}$$

In case (a), if CH_4 is a minor species (as probably intended for this mechanism), the single reaction of the network is contained in the last row, which is the same as reaction (72) in section 7.2.1, and corresponds to the overall reaction stoichiometry in equation (75); that is, $F_s = R = 1$. In case (b), if CH_4 is a major species, the reaction network is contained in the last 2 rows, and these are equivalent to reactions (73) and (74) in section 7.2.1 (with (86=(73) - (74)), or to the overall stoichiometry of equations (76) and (77), with the equation corresponding to (86) given by (76) - (77); that is, $F_s = R = 2$.

7.3 Stoichiometric Restrictions

In this tutorial, as a general introduction to CRS, we assume that there are no restrictions on the allowable changes in composition on reaction other than the atom-balance constraints. This means that $F_s = R$. However, the composition of a reacting system may be further restricted in ways that stoichiometry itself cannot predict (but it can take such restrictions into account, see below). For example, with $R > 1$, two reactants may combine in a particular ratio, or a particular reaction may effectively be prevented from taking place by lack of an appropriate catalyst. We refer to any such restriction as a *stoichiometric restriction*, and its existence can only be discovered by experiment. Each stoichiometric restriction has the effect of reducing F_s by 1, but has no effect on R, which refers to the general (unrestricted) solution. If r is the number of stoichiometric restrictions,

$$F_s = R - r = N - C - r \tag{88}$$

Once the number and nature of the r stoichiometric restrictions are known, a stoichiometric analysis can proceed as described in this tutorial by appropriate modification of the system formula matrix. The procedure is described by Smith and Missen (1982, 1991, *pp.* 29–36)

7.4 From Chemical Equations to Atom-balance Equations

Just as a proper set of chemical equations can be generated from a given formula matrix, a (proper) formula matrix can also be generated from a given set of chemical equations. This is useful if the only information available concerning a system is in the form of a such a set of chemical equations. This set of equations corresponds to a given *stoichiometric matrix*. The mathematical basis is the same in both cases (whether starting from a formula matrix or from a stoichiometric matrix). The procedure is described by Smith and Missen (1982, 1991, section 2.4.5).