Identification and Application of Partial Chemical Equilibria in Reactor Modeling

Graeme W. Norval
ICI Canada Inc., Sheridan Park Research Centre, Mississauga, Ont., Canada L5K 2L3

M. Jane Phillips and Ronald W. Missen
Dept. of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ont., Canada M5S 1A4

William R. Smith
Dept. of Mathematics and Statistics, University of Guelph, Guelph, Ont., Canada N1G 2W1

A method is presented for identifying a subset of species (from a set of reacting species) that are within a specified numerical tolerance of equilibrium, as implied by a given experimental composition. The method also determines a linearly independent set of reactions involving these species and the number of stoichiometric restrictions inherent in the set. This is an aid in reactor modeling, for example, in the computation of concentration profiles, in examining kinetic schemes or reaction mechanisms, and in identifying rate-controlling processes. An example involving the methanol-to-gasoline synthesis is given to illustrate the method.

Introduction

Equilibrium analysis is an important tool in the study of reacting systems (Smith and Missen, 1982, 1988). This has been demonstrated, for example, in two cases involving catalysis by the shape-selective zeolite ZSM-5: alkene and alcohol aromatization (Norval et al., 1989a), and olefin oligomerization (Norval et al., 1989b). Conventional equilibrium analysis, as in these two cases, considers equilibrium with respect to the set of all specified reacting species of a system and all possible chemical reactions (that is, *full* equilibrium). However, in some situations arising in reactor or reaction modeling, *partial* equilibria may exist in which a subset of species attains equilibrium within the larger set of reacting species. Furthermore, equilibrium (whether full or partial) may be *stoichiometrically restricted* in that all possible chemical reactions are not involved (Cheluget et al., 1987). The usefulness of identifying partial equilibria stems from at least two considerations: reduction in the number of rate equations required in reactor modeling, for example, in calculating concentration profiles; and establishing and examining kinetic schemes and reaction mechanisms.

Other workers have found it useful to reduce the number of rate equations in reactor modeling. Ramshaw and Cloutman (1981) have developed a numerical method for computing concentration profiles for "chemically reactive fluid flow," in which some reactions are considered to be at equilibrium and others are not. They have illustrated it by application to modeling the behavior of an internal combustion engine. For use of their method, it is necessary to identify beforehand "which reactions are in equilibrium and which need to be treated kinetically." They discuss this in terms of "fast" and "slow" reactions, the former being considered to be at equilibrium. (They point out that there would be at least a short initial period in which the equilibrium assumption would not be valid.) Instead of a *rate* criterion, we consider and implement here an *equilibrium* criterion based on an analysis of experimental data.

The system may be multiphase and not just single-phase as above. For example, Glasscock and Rochelle (1989), in simulating numerically the absorption of CO_2 by aqueous diethanolamine, as in a packed tower reactor, have used equilibrium in the bulk liquid as a boundary condition in the solution of the diffusion equations for a combined equilibrium/mass-transfer model.

The identification of partial equilibria is also useful in establishing and testing kinetic schemes and reaction mechanisms, which we take to be distinct. A kinetic scheme includes a set of N reacting species observable in the normal analytical sense and a number of reaction steps equal to the maximum

---

Correspondence concerning this article should be addressed to R. W. Missen.

number (R) of linearly independent chemical equations involving the N species. Thus, a kinetic scheme enables calculation of the concentration profiles of the observable species in a reactor through use of a rate equation for each of the steps and the necessary transport equations and other information. A reaction mechanism, on the other hand, usually includes transient species such as free radicals in addition to the N observable species, all of which are involved in a number of elementary steps/processes usually greater than the maximum number of linearly independent steps. Such a mechanism is often less useful (because of lack of sufficient data) for the phenomenological modeling of a reactor, unless it is reduced to a kinetic scheme, as by, inter alia, application of the steady-state hypothesis to the transient species. Equilibrium analysis can deal with either of these situations.

The purpose of this article is to present a method, together with an algorithm for its implementation, that identifies a subset of species at (that is, within a specified numerical precision of) equilibrium for a given system composition. This algorithm tests for equilibrium all possible kinetic schemes (that is, sets of R reactions) for which each reaction step involves at most $N-R+1$ species. It also determines the number of stoichiometric restrictions within the identified subset.

In the following, we first describe quantitatively the distinction between full and partial equilibrium, and that between stoichiometrically unrestricted and restricted systems; this includes the working equations as the basis for the algorithm. Application of the method is illustrated with an example involving the methanol-to-gasoline (MTG) synthesis.

Full and Partial Equilibrium; Stoichiometric Restrictions

Since the method to be presented is based partially on stoichiometric concepts, we first delineate the relevant aspects of the stoichiometric description of a system (which description is independent of any equilibrium considerations). For a system specified by a list of N species, we define the following (Smith and Missen, 1982, Chapter 2). $A=(\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_N)$ is the $M \times N$ formula matrix with elements a_{ki}, where $\mathbf{a}_i$ is the formula vector of species i, M is the number of elements contained in the N species, and a_{ki} is the subscript to element k in the molecular formula of species i. C is the number of components, defined by:

$$C=\mathrm{rank}(A) \tag{1}$$

($C \le M$). $N=(\boldsymbol{\nu}_1, \boldsymbol{\nu}_2, \ldots, \boldsymbol{\nu}_{R'})$ is an $N \times R'$ stoichiometric matrix with elements ν_{ij}, where $\boldsymbol{\nu}_j$ is the stoichiometric vector for chemical equation j, R' is the number of chemical equations (not necessarily linearly independent), and ν_{ij} is the stoichiometric coefficient of species i in equation j. A and N are related by:

$$AN=\mathbf{0} \tag{2}$$

F_s is the number of stoichiometric degrees of freedom, defined by

$$F_s=\mathrm{rank}(\mathbf{N}) \tag{3}$$

Equations 2 and 3 imply

$$F_s \le N-C \equiv R \tag{4}$$

When the equality holds, the system is said to be stoichiometrically *unrestricted*; if, in addition, $R=R'$, N is a *complete* stoichiometric matrix for the system, which we denote by N_c. When the inequality holds, the system is stoichiometrically *restricted*, and the number of stoichiometric restrictions is r, defined by:

$$r=R-F_s \tag{5}$$

Finally, it is useful to consider N_c in *canonical form* (Smith and Missen, 1982, p. 24), which implies that each chemical equation includes at most $C+1$ (that is, $N-R+1$) species. The canonical form of N_c is not unique but depends on the particular choice of C component species. A computer program (in BASIC) for the computation of a N_c in canonical form from A has been given previously (Missen and Smith, 1989), and is incorporated in the algorithm used here.

Full equilibrium involves all N species, whose chemical potentials, $\boldsymbol{\mu}$, satisfy the (equilibrium) criterion:

$$\mathbf{\Delta G} \equiv N_c^T \boldsymbol{\mu} = \mathbf{0} \tag{6}$$

where $\mathbf{\Delta G}$ is the vector of changes in the Gibbs function (free energy) for the R chemical equations. For convenience, in this paper, $\mathbf{\Delta G}$ and $\boldsymbol{\mu}$ are dimensionless (the usual quantities divided by RT, where R is the gas constant and T is the temperature). *Partial* equilibrium involves N_{eq} ($<N$) species whose chemical potentials satisfy Eq. 6.

Our method for identifying species in partial equilibrium makes use of the freedom granted by the nonuniqueness of N_c in canonical form. By selecting different sets of component species, we obtain different sets of equations, corresponding to reaction steps in a kinetic scheme. For each of these sets, we test each of the R resulting reaction steps for equilibrium using the given system composition by means of the criterion:

$$|\Delta G_j| \equiv \left| \sum_{i=1}^{C+j} \nu_{ij}\mu_i \right| \le \epsilon_j; \quad j=1, 2, \ldots, R \tag{7}$$

The value of ϵ_j depends on the precision of the thermodynamic and compositional data used in the calculation of ΔG_j. (The determination of ϵ_j is described below.) In order to test all possible reactions, we must evaluate all possible N_c matrices. Since the number of these may be very large, it is important to devise an efficient algorithm for this evaluation (also described below).

As a result of testing all possible N_c matrices against the equilibrium criterion 7, we identify N_{eq} species involved in the stoichiometric matrix N_{eq}, of order $N_{eq} \times R'_{eq}$, whose columns contain all the reactions identified to be at equilibrium, such that:

$$A_{eq} N_{eq} = \mathbf{0} \tag{8}$$

where A_{eq} is of order $M \times N_{eq}$, and whose columns are, in general, a subset of the columns of A. This establishes whether equilibrium is *full*, with:

$$N_{\mathrm{eq}} = N \qquad (9)$$

or *partial*, with

$$N_{\mathrm{eq}} < N. \qquad (10)$$

We next eliminate linearly dependent reactions from N_{eq} to produce the stoichiometric matrix N^*_{eq}, of order $N_{\mathrm{eq}} \times F_{s,\mathrm{eq}}$, where

$$F_{s,\mathrm{eq}} \equiv \mathrm{rank}(\mathbf{N}_{\mathrm{eq}}) = \mathrm{rank}(\mathbf{N}^*_{\mathrm{eq}}) \qquad (11)$$

The number of stoichiometric restrictions is then

$$r_{\mathrm{eq}} = N_{\mathrm{eq}} - \mathrm{rank}(A_{\mathrm{eq}}) - F_{s,\mathrm{eq}} \geq N_{\mathrm{eq}} - F_{s,\mathrm{eq}} - \mathrm{rank}(\mathbf{A}) \geq 0 \qquad (12)$$

The stoichiometry can then be either unrestricted ($r_{\mathrm{eq}} = 0$) or restricted ($r_{\mathrm{eq}} > 0$).

Equilibrium Criterion for Imprecise Data

In general, for a reaction involving N species, we have

$$\Delta G_j = \sum_{i=1}^{N} \nu_{ij}\mu_i = \sum_{i=1}^{N} \nu_{ij}[\mu_i^* + \ln a_i(x)] \qquad (13)$$

where μ_i^* is the standard chemical potential of species i at (T, P), a_i is the activity of species i, and x is the vector of mole fractions. We wish to test the null hypothesis that $\Delta G_j = 0$. For this purpose, we consider the data μ_i^* and a_i, and hence ΔG_j, as random variables, and assess the "reasonableness" of the measured values, $\Delta G_{j,\mathrm{meas}}$, relative to the null hypothesis, where $\Delta G_{j,\mathrm{meas}}$ is given by Eq. 13 in the form

$$\Delta G_{j,\mathrm{meas}} = \sum_{i=1}^{N} \nu_{ij}\mu_{i,\mathrm{meas}} \qquad (14)$$

$$= \sum_{i=1}^{N} \nu_{ij}[\mu^*_{i,\mathrm{tab}} + \ln a_{i,\mathrm{meas}}] \qquad (15)$$

where subscripts *tab* and *meas* denote values obtained from the data compilation used and from the experiment, respectively. We assume that μ_i^* and $\ln a_i$ are independently normally distributed about their means with variances $\sigma^2_{\mu_i^*}$ and $\sigma^2_{\ln a_i}$. ΔG_j hence follows a normal distribution about its mean with variance $\sigma^2_{\Delta G_j}$. To assign a numerical value to $\sigma^2_{\Delta G_j}$, we further assume that $\sigma^2_{\mu_i^*}$ and $\sigma^2_{\ln a_i}$ are constant, and in accordance with Eq. 15, we may write (Lloyd, 1984, p. 36)

$$\sigma^2_{\Delta G_j} = (\sigma^2_{\mu^*} + \sigma^2_{\ln a}) \sum_{i=1}^{N} \nu_{ij}^2 \qquad (16)$$

The value of $\sigma^2_{\mu^*}$ must be inferred from the indicated precision of the tabulated data. $\sigma^2_{\ln a}$ depends on the explicit form of a, and requires further consideration, as described specifically in the example below, and more generally in the discussion.

We conclude that the hypothesis $\Delta G_j = 0$ is correct at the $100(1-2\alpha)\%$ significance level, that is, the reaction is at equilibrium, if

$$|\Delta G_{j,\mathrm{meas}}| \equiv \left|\sum_{i=1}^{N} \nu_{ij}\mu_{i,\mathrm{meas}}\right| \leq u_\alpha \sigma_{\Delta G_j} \equiv \epsilon_j;\ j = 1, 2, \ldots, R \qquad (17)$$

where u_α is the $100(1-2\alpha)$ percentage point of the normal distribution and $\sigma_{\Delta G_j}$ is defined by Eq. 16 (Lloyd, 1984, pp. 255-6, A18). Criterion 17 thus defines ϵ_j in criterion 7. Finally, substituting Eq. 16 into criterion 17 for a reaction in canonical form, we obtain:

$$\frac{|\Delta G_{j,\mathrm{meas}}|}{\left(\sum_{i=1}^{C+j} \nu_{ij}^2\right)^{1/2}} \leq u_\alpha (\sigma^2_{\mu^*} + \sigma^2_{\ln a})^{1/2} \equiv \epsilon^*; \quad j = 1, 2, \ldots, R \qquad (18)$$

where ϵ^* is a "lumped" equilibrium criterion parameter.

Criterion 18 is applied to a given set of compositional data to calculate N_{eq}, $F_{s,\mathrm{eq}}$ and other quantities, over the "useful range" of values of ϵ^* from 0 to an upper value at which both N_{eq} and $F_{s,\mathrm{eq}}$ have attained their limiting values of N and R, respectively. (For larger values of ϵ^*, the system would be determined to be at full unrestricted equilibrium.) Determining this useful range involves exploration of ϵ^* over a range of values $\{k\Delta\epsilon^*;\ k = 1, 2, \ldots,\}$ using the algorithm described below.

The results of the dependence of the various quantities on ϵ^* can then be used to infer the combinations of u_α and σ^2 values which are relevant to determining the extent of equilibrium in the system (for the given composition). This can range from complete kinetic control ($N_{\mathrm{eq}} = 0$) through partial equilibrium (with or without restrictions) to full restricted equilibrium ($N_{\mathrm{eq}} = N$, $F_{s,\mathrm{eq}} = R$).

The use of the algorithm and the interpretation of its results are illustrated in the example given below.

Algorithm

The set of all possible reactions in canonical form can be generated by selecting C species (columns of A) followed by reduction of A to unit matrix form, and testing the resulting $(N-C)$ reactions for each selection. The total number of such reactions is given by $N!/[(C+1)!(N-C-1)!]$, which is the number of ways of selecting $C+1$ items from a list of N items.

We implement this section systematically as follows. For each set of C species, we create a working matrix $\boldsymbol{B}$; the first C columns of $\boldsymbol{B}$ are the formula vectors for the C selected species $(\boldsymbol{a}_{i_1}, \boldsymbol{a}_{i_2}, \ldots, \boldsymbol{a}_{i_C})$, where $i_1 < i_2, \ldots, < i_C$; the remaining columns of $\boldsymbol{B}$ are the formula vectors $\{\boldsymbol{a}_k\}$, where $k > i_C$. Initially, the first C columns of $\boldsymbol{B}$ are selected as $(\boldsymbol{a}_1, \boldsymbol{a}_2, \ldots, \boldsymbol{a}_C)$, that is, $\boldsymbol{B} = A$; subsequently, $\boldsymbol{B}$ has fewer columns than A, and $\boldsymbol{B}$ ultimately becomes the matrix $(\boldsymbol{a}_{N-C}, \boldsymbol{a}_{N-C+1}, \ldots, \boldsymbol{a}_N)$.

The number of reactions tested can often be reduced from the above number as follows. For any given set of C species with formula matrix A_C, $C \geq \mathrm{rank}(A_C)$. For many cases, $C = \mathrm{rank}(A_C)$ for any selection of C species, and the number of reactions that must be tested is given above. When $C > \mathrm{rank}(A_C)$ for some selection of C species, we need only check the reaction involving the initial rank $(A_C) + 1$ species in $\boldsymbol{B}$ prior to proceeding to the next set of C species. All other possible reactions with these rank (A_C) species would be identified in a subsequent test.

The steps in the algorithm and the resulting output are as follows:

1. Enter the data: $\boldsymbol{A}$, μ_{meas}, and $\Delta\epsilon^*$ (for example, $\Delta\epsilon^* = 0.001$). Set $\epsilon^* = \Delta\epsilon^*$.
2. Select M species as a tentative set of components, and hence form an initial $\boldsymbol{B}$.
3. Reduce $\boldsymbol{B}$ to unit matrix form to generate a set of R linearly independent chemical equations forming a complete stoichiometric matrix, N_c, in canonical form. A byproduct of this is the determination of $C = \text{rank}(A)$.
4. If criterion 18 is satisfied, check if the reaction has been previously identified; if not, store it in N_{eq} and proceed to the next reaction in N_c.
5. If criterion 18 is not satisfied, proceed to the next reaction in N_c.
6. Repeat steps 2 to 5 until all possible sets of M species have been tested.
7. Determine N^*_{eq}, $F_{s,\text{eq}}$, and rank (A_{eq}).
8. Print the results. The output contains the following:
   the value of ϵ^*;
   either:
   "there are no reactions in canonical form satisfying the equilibrium criterion" (if criterion 18 is unsatisfied for all possible sets of M component species).
   or:
   - The reactions as identified, corresponding to N_{eq}.
   - The statement "This is a case of full/partial unrestricted/restricted equilibrium".
   - The matrix N^*_{eq} in canonical form.
   - The number of reactions actually tested.
   - The values of: N, $C = \text{rank}(A)$, R'_{eq}, N_{eq}, $\text{rank}(A_{\text{eq}})$, $F_{s,\text{eq}}$.
9. If $N_{\text{eq}} < N$ or $F_{s,\text{eq}} < R$, set $\epsilon^* = \epsilon^* + \Delta\epsilon^*$ and repeat steps 2 to 8.

A computer program written in BASIC implementing this algorithm is available from the authors.

Example

To illustrate an application of this method, we consider the MTG synthesis. The chemistry and catalysis of MTG have been reviewed by Chang (1983). Methanol is converted to a mixture of $C_6 - C_{10}$ aromatic and $C_1 - C_{10}$ aliphatic hydrocarbons and water over zeolite H-ZSM-5 at temperatures between 650 and 800 K and pressures between 0.1 and 2.5 MPa.

We have tested the product distributions reported by Yurchak et al. (1979, Tables III and IV) for partial equilibria using criterion 18. These data were obtained at ≈700 K and 2.1 MPa for 6 cases: for two values of time-on-stream (tos) for each of 3 cases (fresh catalyst, six-times regenerated catalyst, and nine-times regenerated catalyst). The minimum reported yield was 0.1 wt. %; thus only species with greater yields are included in our species list.

In applying the method presented herein, we obtained the thermodynamic data for the alkanes and the alkenes from Alberty and Gehrig (1984 and 1985, respectively), those for the cycloalkanes from Alberty and Ha (1985), those for the aromatics from Alberty (1985), and those for H_2O, CO, CO_2, CH_3OH and $(CH_3)_2O$ from Stull et al. (1969). In criterion 18, the chemical potential of each species was calculated from

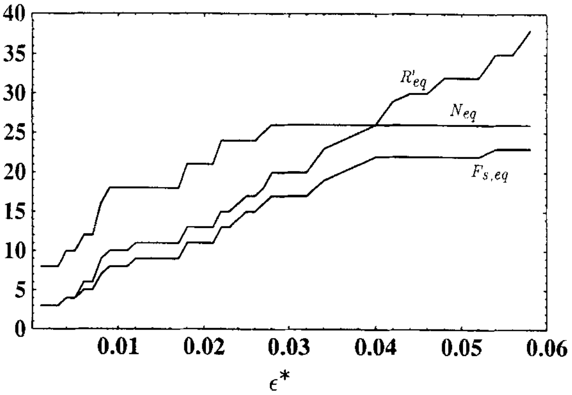

Figure 1. R'_{eq}, N_{eq}, and $F_{s,\text{eq}}$ as a function of ϵ^* in criterion 18, for Case 6 of Yurchak et al. (1979).

$N = 26$, $R = 23$, $\text{rank}(A) = 3$.

$$\mu_i = \mu_i^0(T) + \ln P + \ln x_i \equiv \mu_i^* + \ln x_i \tag{19}$$

where μ_i^0 is the standard chemical potential, P is the pressure, and x_i is the mole fraction. The program was run on a Dell 425E computer with a Weitek 4167 (25MHz) co-processor running MS-DOS, using the QuickBasic 4.5 compiler. For the case described below, the execution time was 5.5 min, using $\Delta\epsilon^* = 0.001$.

Figure 1 shows the dependence of the results on ϵ^* for Case 6 of Yurchak et al. (1979). As ϵ^* increases, N_{eq} approaches $N(=26)$, $F_{s,\text{eq}}$ approaches $F_s(=23)$, and R'_{eq} increases (eventually approaching the value $N!/[(C+1)!(N-C-1)!] = 14{,}950$). For $\epsilon^* > 0.028$, the system of 26 species is determined to be in full equilibrium for at least one kinetic scheme. For $\epsilon^* < 0.028$, the system is in partial equilibrium. Since $\text{rank}(A_{\text{eq}}) = 3$ and Figure 1 shows that $N_{\text{eq}} - F_{s,\text{eq}} > 3$ for $\epsilon^* < 0.054$, stoichiometric restrictions are present up to this value.

To illustrate the implications of the results of Figure 1 for the precision of the experimental data, we take $u_\alpha = 1.960$, corresponding to the 95% significance level, and $\sigma_{\mu^*} = 0.001$, inferred from the tabulated data. Then, criterion 18 implies: if $\sigma_{\ln a} > 0.027$ (corresponding to $\epsilon^* > 0.054$), the data are not sufficiently precise to indicate anything other than full unrestricted equilibrium; if $0.027 > \sigma_{\ln a} > 0.014$ (the latter corresponding to $\epsilon^* = 0.028$), the data can only indicate full equilibrium with restrictions. If the data are sufficiently precise ($\sigma_{\ln a} < 0.014$), partial restricted equilibrium is indicated and further analysis is warranted.

To illustrate such a further analysis, we consider $\epsilon^* = 0.020$, corresponding to $\sigma_{\ln a} = 0.01$. Table 1 lists the 13 (R'_{eq}) reactions identified, corresponding to N_{eq}, involving $N_{\text{eq}} = 21$ species; of these, only 11 ($F_{s,\text{eq}}$) are linearly independent, corresponding to N^*_{eq}.

Using $\epsilon^* = 0.020$ for the other five cases of Yurchak et al. (1979), we have identified reactions at equilibrium using criterion 18. The results for all 6 cases are summarized in Table 2. Each case illustrates partial ($N_{\text{eq}} < N$), restricted ($r_{\text{eq}} > 0$) equilibrium. For all 6 cases tested, nearly all the reactions identified as being at equilibrium involve isomerization, alkylation, or transalkylation of aromatics. These results may be used to examine reported kinetic schemes.

Table 1. Partial Equilibria in MTG Synthesis* (Case 6, Yurchak et al., 1979)

$$\begin{aligned}
4H_2O+7C_6H_6 &= 5(CH_3)_2C_6H_4+2CO_2\\
(CH_3)_3C_6H_3 &= (C_3H_7)C_6H_5\\
4C_2H_6 &= n-C_5H_{12}+3CH_4\\
2n-C_4H_{10} &= C_6H_{14}+C_2H_6\\
3C_2H_6+16(CH_3)_3C_6H_3 &= 15\ 1,2,3,5(CH_3)_4C_6H_2\\
3C_2H_6+16(C_3H_7)C_6H_5 &= 15\ 1,2,3,5(CH_3)_4C_6H_2\\
3n-C_4H_{10}+22(CH_3)(C_2H_5)C_6H_4 &= 21C_{10}H_{14}\\
27C_4H_8 &= 4(C_3H_7)C_6H_5+12C_6H_{14}\\
27C_4H_8 &= 4(CH_3)_3C_6H_3+12C_6H_{14}\\
6i-C_5H_{12}+25(CH_3)_2C_6H_4 &= 23\ 1,2,3,4(CH_3)_4C_6H_2\\
4C_5H_{10}+5C_6H_6 &= 5\ 1,2,3,4(CH_3)_4C_6H_2\\
26c-C_5H_{10} &= 5(C_2H_5)C_6H_5+15C_6H_{14}\\
3C_7H_8 &= (CH_3)(C_2H_5)C_6H_4+2C_6H_6
\end{aligned}$$

The 6th and 9th reactions are linearly dependent on the remainder

*$\epsilon^* = 0.020$

Dejaifve et al. (1980) performed a series of kinetics experiments and, based on their results and their review of the literature, proposed three kinetic schemes for the various stages of the MTG process. The first two of these could not be examined by our method, because of lack of reported data. Scheme III of Dejaifve et al. provides a mechanism for the formation of aromatics and alkanes from alkenes. They suggested that toluene and the xylenes are the initial aromatics species (formed following dehydrogenation and cyclization of C_7 and C_8 alkenes), and that alkylation and transalkylation reactions lead to the variety of aromatics species produced.

Our calculations indicate that nearly all the reactions identified as being at equilibrium involve aromatics, and that the alkenes are not at equilibrium. This, together with the essentialy complete conversion of methanol, suggests that alkene disproportionation and subsequent aromatics formation reactions equilibrate slowly, and hence are possibly rate-determining. However, alkene disproportionation reactions equilibrate rapidly in the absence of aromatics (Tabak, 1981), and would not be rate-determining under such circumstances. Given that aromatics are more strongly adsorbed on H-ZSM-5 than are alkenes and alkanes (Wolthuizen et al., 1980), alkene equilibration on the acid sites would be retarded by the adsorbed aromatics. Hence, possible rate-determining steps are aromatics formation on, and their desorption from, the acid sites. This also suggests that increased aromatics yields would be promoted by removing them rapidly from the catalyst.

Discussion

The method presented herein provides, via criterion 18, a means of identifying subsets of species which are in equilibrium within a set of reacting species. This general equilibrium criterion also provides a means of determining a range of ϵ^* values for which useful observations can be made concerning the data. For larger ϵ^* values all the system species would be determined to be at equilibrium, thus providing no kinetic insight.

Table 2. Summary of Partial Equilibrium Analysis with $\epsilon^* = 0.020$ for Cases* (MTG) of Yurchak et al. (1979)

Case	tos/h	Cat. Regen.	N	N_{eq}	rank(A_{eq})	$F_{s,eq}$	r_{eq}
1	73	0	28	23	3	16	4
2	94	6	26	20	3	14	3
3	77	9	27	25	3	16	6
4	314	0	29	22	3	18	1
5	333	6	27	21	3	13	5
6	316	9	26	21	3	11	7

*$M = 3 = \text{rank}(A) \equiv C$, for all six cases; $T = 700$ K; $P = 2.1$ MPa

From another point of view, the method may also be used as an aid in the interactive design of kinetics experiments. By this we mean that it may be used to obtain an indication of the experimental precision required to draw conclusions regarding the extent to which the system is kinetically controlled. This is possible using criterion 18 when u_α and σ_{μ^*} are known. First, a preliminary set of kinetic data would be analyzed to calculate information equivalent to that in Figure 1. Sets of $\{u_\alpha, \sigma_{\ln a}\}$ which would yield partial equilibrium could then be determined. If the resulting values of $\sigma_{\ln a}$ are smaller than the value relevant to the preliminary data, further experiments would then be performed with increased precision.

A further use of this algorithm would be to establish that partial equilibrium exists in order to reduce the number of rate equations required for calculating temperature and concentration profiles in a reactor. At certain points in space/time, the algorithm could be applied to experimentally measured compositions to determine the extent to which partial equilibrium has been established. The investigator can use this information to reduce the number of rate equations required for modeling subsequent reactor segments/time.

Finally, our method may be used to help develop kinetic schemes. For example, a series of experiments could be performed at increasing extents of conversion. By applying our analysis following each experiment, the "fast" reactions, those which rapidly approach equilibrium, and the "slow" reactions, those which approach equilibrium only slowly, may be identified. Through this means, the rate-determining steps may be identified. In addition, as illustrated by the MTG example, identification of these steps can also provide useful insight for existing kinetic schemes.

A computer program written in BASIC implementing this algorithm is available from the authors.

Acknowledgment

Financial support has been received from the Natural Sciences and Engineering Research Council of Canada.

Notation

a_i = activity of species i
a_{ki} = subscript to element k in the molecular formula of species i
$\mathbf{a}_i$ = formula vector of species i
$\mathbf{A}$ = $(M \times N)$ formula matrix
$\mathbf{B}$ = working matrix in the algorithm (see text)
C = rank $(\mathbf{A})$, number of components
F_s = number of stoichiometric degrees of freedom
ΔG_j = change in Gibbs function (free energy) for chemical equation j, dimensionless
$\mathbf{\Delta G}$ = vector of changes in Gibbs function, dimensionless
M = number of elements
MTG = methanol-to-gasoline synthesis (process)
N = number of reacting species
$\mathbf{N}$ = stoichiometric matrix
$\mathbf{N}_c$ = complete stoichiometric matrix
$\mathbf{N}^*_{eq}$ = stoichiometric matrix of order $N_{eq} \times F_{s,eq}$

P = pressure, MPa
r = number of stoichiometric restrictions
R = maximum number of linearly independent chemical equations = $N-\text{rank}(A)$; gas constant, 8.314 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
R' = number of columns in matrix N; number of chemical equations
tos = time on stream, h
T = temperature, K
u_α = $100(1-2\alpha)$ percentage point of the normal distribution
x_i = mole fraction of species i
x = vector of mole fractions

Greek letters

α = statistical significance level
ϵ_j = parameter for distinguishing equilibrium and nonequilibrium in criteria 7 and 17, dimensionless
ϵ^* = parameter for distinguishing equilibrium and nonequilibrium in criterion 18
$\Delta\epsilon^*$ = increment in ϵ^* in algorithm, dimensionless
μ_i = chemical potential of species i, dimensionless
μ_i^0 = standard chemical potential of species i, function of T, dimensionless
μ_i^* = standard chemical potential of species i, function of (T, P), dimensionless
μ = vector of chemical potentials, dimensionless
ν_{ij} = stoichiometric coefficient of species i in chemical equation j
ν_j = stoichiometric vector for chemical equation j
σ = standard deviation (in, with subscript)
σ^2 = variance (of, with appropriate subscript)

Subscripts

eq = at equilibrium
i, j, k = dummy indices
meas = measured
tab = tabulated

Superscript

T = transposed vector or matrix

Literature Cited

Alberty, R. A., "Standard Chemical Thermodynamic Properties of Alkylbenzene Isomer Groups," *J. Phys. Chem. Ref. Data*, **14**, 177 (1985).

Alberty, R. A., and C. A. Gehrig, "Standard Chemical Thermodynamic Properties of Alkane Isomer Groups," *J. Phys. Chem. Ref. Data*, **13**, 1173 (1984).

Alberty, R. A., and C. A. Gehrig, "Standard Chemical Thermodynamic Properties of Alkene Isomer Groups," *J. Phys. Chem. Ref. Data*, **14**, 803 (1985).

Alberty, R. A., and S. Ha, "Standard Chemical Thermodynamic Properties of Alkylcyclopentane Isomer Groups, Alkylcyclohexane Isomer Groups and Combined Isomer Groups," *J. Phys. Chem. Ref. Data*, **14**, 1107 (1985).

Chang, C. D., "Hydrocarbons from Methanol," *Cat. Rev.-Sci. Eng.*, **25**, 1 (1983).

Cheluget, E. L., R. W. Missen, and W. R. Smith, "Computer Calculation of Ionic Equilibria Using Species- or Reaction-Related Thermodynamic Data," *J. Phys. Chem.*, **91**, 2428 (1987).

Dejaifve, P., J. C. Vedrine, V. Bolis, and E. G. Derouane, "Reaction Pathways for the Conversion of Ethanol and Olefins on H-ZSM-5 Zeolite," *J. Cat.*, **63**, 331 (1980).

Glasscock, D. A., and G. J. Rochelle, "Numerical Simulation of Diffusion and Reversibility Effects on CO_2 Absorption into Aqueous Diethanolamine," AIChE Meeting, Houston (Apr. 4, 1989).

Lloyd, E., ed., *Handbook of Applicable Mathematics: Vol. VI, Part A, Statistics*, Wiley-Interscience, New York (1984).

Missen, R. W., and W. R. Smith, "A Question of Basic Chemical Literacy?," *J. Chem. Educ.*, **66**, 217 (1989); erratum, **66**, 534 (1989).

Norval, G. W., M. J. Phillips, R. W. Missen, and W. R. Smith, "Calculated Equilibria for the Alkene and Alcohol Aromatization Processes," *Appl. Cat.*, **54**, 35 (1989a).

Norval, G. W., M. J. Phillips, R. W. Missen, and W. R. Smith, "On Chemical Equilibrium of Pseudo-One-Element Systems: Application to Oligomerization," *Can. J. Chem. Eng.*, **67**, 652 (1989b).

Ramshaw, J. D., and L. D. Cloutman, "Numerical Method for Partial Equilibrium Flow," *J. Comput. Phys.*, **39**, 405 (1981).

Smith, W. R., and R. W. Missen, *Chemical Reaction Equilibrium Analysis: Theory and Algorithms*, Wiley-Interscience, New York (1982).

Smith, W. R., and R. W. Missen, "Strategies for Solving the Chemical Equilibrium Problem and an Efficient Microcomputer-based Algorithm," *Can. J. Chem. Eng.*, **66**, 591 (1988).

Stull, D. R., E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York (1969).

Tabak, S. A., "Production of Synthetic Diesel Fuel From Light Olefins," U.S. Patent 4,254,295 (1981).

Wolthuizen, J. P., J. P. van den Berg, and J. H. C. van Hooff, in *Studies in Surface Science and Catalysis, Vol. 5, Catalysis by Zeolites*, p. 85, B. Imelik, C. Naccache, Y. Ben Taarit, J. C. Vedrine, G. Coudurier, and H. Praliud, eds., Elsevier, Amsterdam (1980).

Yurchak, S., S. E. Voltz, and J. P. Warner, "Process Aging Studies in the Conversion of Methanol to Gasoline in Fixed Bed Reactor," *Ind. Eng. Chem. Proc. Des. Dev.*, **18**, 527 (1979).

Manuscript received Jan. 13, 1992, and revision received Apr. 13, 1992.