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THE NUMERICAL INTEGRATION OF KINETIC EQUATIONS FOR CHEMICAL SYSTEMS HAVING BOTH SLOW AND FAST REACTIONS

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SUMMARY

A method is presented which speeds up the integration of kinetic equations for chemical systems having widely variant reaction rates. An algorithm is given for finding the conservation equations for a chemical system. An example is analyzed in detail using the given techniques.

THE NUMERICAL INTEGRATION OF KINETIC EQUATIONS FOR CHEMICAL SYSTEMS HAVING BOTH SLOW AND FAST REACTIONS

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1. Reactions in an Ideal Gas

Let $A_1, A_2, \ldots, A_N$ be the substances present in an ideal gas. For example, if the gas contains water, hydrogen and oxygen, then N = 3 and we may let

$$A_1 = H_2 , \quad A_2 = O_2 , \quad A_3 = H_2O .$$

Let x_j be the number of moles of A_j present in the gas. Let $\hat{x}_j$ be the mole-fraction of the substance A_j present, where

$$(1.1) \qquad \hat{x}_j = \frac{x_j}{\sum_{j=1}^{N} x_j} .$$

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Denote the denominator of Eq. (1.1) by σ, i.e., let

$$\sigma = \sum_{j=1}^{N} x_j$$

be the total number of moles of all substances in the gas.

Consider a chemical reaction

$$\sum_{j=1}^{N} m_j A_j \underset{k'}{\overset{k}{\rightleftharpoons}} \sum_{j=1}^{N} n_j A_j \ .$$

This notation means that m_1 molecules of substance A_1 react with m_2 molecules of substance A_2, etc., to form n_1 molecules of substance A_1, n_2 molecules of A_2, etc. For example, the reaction

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$

would have

$$m_1 = 2 \qquad n_1 = 0$$

$$m_2 = 1 \qquad n_2 = 0$$

$$m_3 = 0 \qquad n_3 = 2$$

in the example given above. At constant temperature and pressure, the rate of change of the number of moles of x_j, denoted $\dot{x}_j$, in an ideal gas is assumed to be given by the equation [1]

$$\dot{x}_j = \sigma \left(k \prod_{i=1}^{N} \hat{x}_i^{m_i} - k' \prod_{i=1}^{N} \hat{x}_i^{n_i} \right) \left(n_j - m_j \right) . \tag{1.2}$$

In the above example, this would be

$$\dot{x}_1 = - 2\sigma \left(k\hat{x}_1^2\hat{x}_2 - k'\hat{x}_3^2 \right) ,$$

$$\dot{x}_2 = - \sigma \left(k\hat{x}_1^2\hat{x}_2 - k'\hat{x}_3^2 \right) ,$$

$$\dot{x}_3 = 2\sigma \left(k\hat{x}_1^2\hat{x}_2 - k'\hat{x}_3^2 \right) .$$

When there is more than one reaction, say s reactions, we will use a second subscript on m and n and write

$$\sum_{j=1}^{N} m_{\ell j} A_j \underset{k'_\ell}{\overset{k_\ell}{\rightleftharpoons}} \sum_{j=1}^{N} n_{\ell j} A_j . \qquad \ell=1,2,\ldots,s \tag{1.3}$$

The quantities k_ℓ are the forward reaction rates and the quantities k'_ℓ are the backward reaction rates. The

direction chosen to be forward is arbitrary. The analogous rate equations are

$$\dot{x}_j = \sum_{\ell=1}^{s} f_\ell \left(k_\ell \prod_{i=1}^{N} \hat{x}_i^{m_{\ell i}} - k'_\ell \prod_{i=1}^{N} \hat{x}_i^{n_{\ell i}} \right) \left(n_{\ell j} - m_{\ell j} \right) \tag{1.4}$$

where $f_\ell = \sigma$ for an ideal gas.

2. Multi-phase Systems

Substances in a homogeneous mixture frequently react very similarly to an ideal gas, particularly if the mixture is a dilute solution. Also, when a heterogeneous system consists of a finite number of homogeneous phases, the ideal gas equations can frequently be used as an approximation to each phase. For example, let A_1, A_2, and A_3 be the gas phase substances in a system, and let A_4 = dissolved H_2, A_5 = dissolved O_2, and A_6 = liquid H_2O; i.e., A_4, A_5, and A_6 are the substances in a second (liquid) phase that exists along side of a gas phase consisting of A_1, A_2, and A_3. Then we let

$$\sigma_1 = x_1 + x_2 + x_3$$

and

$$\sigma_2 = x_4 + x_5 + x_6$$

be the total number of moles in phases 1 and 2, respectively. The mole fractions, $\hat{x}_j$, are now defined to be

$$\hat{x}_j = \frac{x_j}{\sigma_1} \qquad j=1,2,3$$

and

$$\hat{x}_j = \frac{x_j}{\sigma_2} \qquad j=4,5,6 \ .$$

For the general case, let p be the number of phases in the system and let $<1>,<2>,\ldots,<p>$ be sets of numbers so that A_j is in phase k if and only if j is in the set $<k>$. Hence $<1>,<2>,\ldots,<p>$ is a <u>partition</u> of the set of integers $\{1,2,3,\ldots,N\}$. Denote by $[j]$ the phase that A_j is in; hence $j\epsilon<k>$ if and only if $k = [j]$. The number of moles in phase k is then

$$\sigma_k = \sum_{j\epsilon<k>} x_j \ , \tag{2.1}$$

and the mole-fraction of substance A_j is

$$\hat{x}_j = \frac{x_j}{\sigma_{[j]}} \quad . \tag{2.2}$$

The general reaction may still be expressed as Eq. (1.3), and the general rate equation as Eq. (1.4). A distinction, however, must be made between an interphase and an intraphase reaction. Reaction ℓ is called* "intraphase k" if for every j such that $[j] \neq k$ we have $m_{\ell j} = 0$ and $n_{\ell j} = 0$. This means that all substances in reaction ℓ are in phase k. In the rate equation (1.4), if reaction ℓ is intraphase k, we would use $f_\ell = \sigma_k$, since reaction ℓ is not influenced by phases other than phase k.

3. Interphase Reactions

An interphase reaction involves substances occurring in more than one phase. For example,

$$H_2O(\text{gas}) \rightleftharpoons H_2O(\text{liquid})$$

*k is used both as a running index on the phases and as a reaction rate. The use should be clear from the context.

would be a reaction involving the evaporation and the condensation of water, and would be written in the above notation as

$$A_3 \rightleftarrows A_6 \ .$$

While certain reactions might, in theory, involve more than two phases, in practice a reaction involving three or more phases could be broken down into simpler reactions involving only one or two phases. We assume here that all interphase reactions involve exactly two phases and we will designate, when necessary, a reaction that occurs between phases k_1 and k_2 as interphase (k_1,k_2), where k_1 and k_2 are an unordered pair of phases. Also, ordinarily, only one substance in each phase will be involved in an interphase reaction, as a reaction of the type

$$2A_3 \rightleftarrows 2A_4 + A_5$$

would ordinarily be written as an interphase reaction

$$A_3 \rightleftarrows A_6$$

followed by an intraphase reaction

$$2A_6 \rightleftharpoons 2A_4 + A_5 \ .$$

For the typical interphase reaction, ℓ, we might expect that exactly one $m_{\ell j}$ is non-zero and exactly one $n_{\ell j}$ is non-zero, the appropriate j being respectively in phases k_1 and k_2. The rate equation would still take the form (1.4), and if we let α be the subscript of the substance in phase k_1 and β be the subscript of the substance in phase k_2, then the ℓ^{th} term of the sum in Eq. (1.4) takes the form

$$(3.1) \qquad \begin{cases} - f_\ell \left(k_\ell \, \hat{x}_\alpha^{m_{\ell\alpha}} - k'_\ell \, \hat{x}_\beta^{n_{\ell\beta}} \right) m_{\alpha\ell} & j=\alpha \\ + f_\ell \left(k_\ell \, \hat{x}_\alpha^{m_{\ell\alpha}} - k'_\ell \, \hat{x}_\beta^{n_{\ell\beta}} \right) n_{\beta\ell} & j=\beta \\ 0 \ . & j\neq\alpha \quad \text{and} \quad j\neq\beta \ . \end{cases}$$

We would normally identify the quantity f_ℓ with the <u>surface area</u> between phases k_1 and k_2; we need only determine either f_ℓ or k_ℓ and k'_ℓ up to a constant and define the other term appropriately. For example, 1) if a

two-phase system consists of a liquid in a test tube and gas above it, we may take $f_\ell = 1$; 2) if phase 1 is a gas bubble and phase 2 is the surrounding liquid, then $f_\ell = \sigma_1^{2/3}$; 3) if phase 1 consists of many bubbles of the same size and phase 2 is the surrounding liquid, take $f_\ell = \sigma_1$; and 4) if phase 1 is a blood vessel, that is, a long thin variable diameter constant length tube (under constant pressure) and again phase 2 is the surrounding liquid, then take $f_\ell = \sqrt{\sigma_1}$.

4. Integration of the Simplest Problem

The simplest (non-trivial) problem is a one-phase system with the single reaction

$$A_1 \underset{k'}{\overset{k}{\rightleftarrows}} A_2 .$$

The rate equations (1.2) are

$$\dot{x}_1 = \sigma(kx_1 - k'x_2)(-1)$$

and

$$\dot{x}_2 = \sigma(kx_1 - k'x_2) ,$$

where $\sigma = x_1 + x_2$. Since $\dot{x}_1 + \dot{x}_2 = 0$, $\dot{\sigma} = 0$. We may normalize by taking $\sigma = 1$ and $x = x_1$ and $x_2 = 1 - x_1 = 1 - x$. Thus,

$$\dot{x} = - kx + k'(1 - x) = k' - (k + k')x \ ,$$

which has the solution

$$x(t) = \frac{k'}{k + k'} + \left(x(0) - \frac{k'}{k + k'} \right) e^{-(k + k')t} \ .$$

Also,

$$\lim_{t \to \infty} x(t) = \frac{k'}{k + k'}$$

and

$$\lim_{t \to \infty} \frac{x_1(t)}{x_2(t)} = \lim_{t \to \infty} \frac{x(t)}{1 - x(t)} = \frac{k'}{k} \ .$$

The <u>quotient</u> of k' and k determines the equilibrium concentration ratio, while the <u>sum</u> of k' and k determines the rate at which equilibrium is attained. If both k' and k are multiplied by a constant greater than unity,

the equilibrium concentration ratio remains the same but the reaction becomes faster.

5. Fast Reactions

The ℓ^{th} reaction of Eq. (1.4) is in equilibrium when

$$(5.1) \qquad k_\ell \prod_{i=1}^{N} \hat{x}_i^{m_{\ell i}} - k'_\ell \prod_{i=1}^{N} \hat{x}_i^{n_{\ell i}} = 0 \ ,$$

that is, when

$$(5.2) \qquad \prod_{i=1}^{N} \hat{x}_i^{m_{\ell i}-n_{\ell i}} = \frac{k'_\ell}{k_\ell} \ .$$

In this form, only $m_{\ell i} - n_{\ell i}$ and k'_ℓ/k_ℓ are of interest, so that we need only to determine these quantities and not their component parts. Let us define

$$(5.3) \qquad r_{\ell i} = m_{\ell i} - n_{\ell i}$$

and

$$(5.4) \qquad h_\ell = \frac{k'_\ell}{k_\ell}$$

so that we can write Eq. (5.2) as

$$\prod_{i=1}^{N} \hat{x}_i^{r_{\ell i}} = h_\ell \quad . \tag{5.5}$$

If reaction ℓ is a reaction so fast that it is effectively always in equilibrium, we set the time derivative of the left side of Eq. (5.5) to zero:

$$\sum_{i=1}^{N} r_{\ell i} \frac{\dot{\hat{x}}_i}{\hat{x}_i} = 0 \tag{5.6}$$

where the expression is valid if and only if all $\hat{x}_i > 0$. $\dot{\hat{x}}_i$ may be expressed in terms of $\dot{x}_i$ by

$$\frac{\dot{\hat{x}}_i}{\hat{x}_i} = \frac{\dot{x}_i}{x_i} - \frac{\dot{\sigma}_{[i]}}{\sigma_{[i]}} \qquad i=1,2,\ldots,N \tag{5.7}$$

where

$$\sigma_{[i]} = \sum_{j \epsilon <[i]>} x_j \tag{5.8}$$

and

$$\dot{\sigma}_{[i]} = \sum_{j \epsilon <[i]>} \dot{x}_j \quad . \tag{5.9}$$

6. Systems with Both Fast and Slow Reactions

Theoretically, for any system, Eq. (1.3), we may numerically integrate [5] Eq. (1.4) to any desired time in order to determine the values for x_j at any time, beginning with the known starting values for x_j. However, one of the drawbacks to numerical integration is that some of the reactions may be very slow and others may be very fast. If this is the case, the time step that can be traversed in one iteration of the numerical integration will be essentially determined by the fastest reaction. This means that, in a very large number of integration steps, nothing very interesting will occur in the slow reactions, which may be the only reactions of interest.

In order to overcome this difficulty, we may approximate the fast reactions by instantaneous reactions of the form Eq. (5.6). Let us suppose that we have s slow reactions and f fast reactions. At this point, we know that the rate of change of x_j, due to the slow reactions only, is given by Eq. (1.4). We now note--and this is the main point of this section--that the fast reactions must react just enough to satisfy Eq. (5.6). Stated mathematically, if we let

$$(6.1) \qquad u_j = \sum_{\ell=1}^{s} f_\ell \left(k_\ell \prod_{i=1}^{N} \hat{x}_i^{m_{\ell i}} - k'_\ell \prod_{i=1}^{N} \hat{x}_i^{n_{\ell i}} \right) \left(n_{\ell j} - m_{\ell j} \right)$$

be the rate of change (by Eq. (1.4)) of x_j contributed by the slow reactions, then there exist numbers $\alpha_1, \alpha_2, \ldots, \alpha_f$, depending on time, such that

$$(6.2) \qquad \dot{x}_j = u_j + \sum_{\ell=1}^{f} r_{\ell j} \, \alpha_\ell$$

AND Eq. (5.6) holds. If we substitute Eq. (6.2) in Eq. (5.6), we get f linear equations in the f unknowns, $\alpha_1, \alpha_2, \ldots, \alpha_f$

$$(6.3) \qquad \sum_{\ell=1}^{f} v_{h\ell} \, \alpha_\ell = g_h \qquad\qquad h=1,2,\ldots,f$$

where

$$(6.4) \qquad v_{h\ell} = \sum_{j} \left[\left(\frac{r_{hj}}{x_j} - \frac{\sum_{i \in \langle [j] \rangle} r_{hi}}{\sigma_{[j]}} \right) r_{j\ell} \right] \qquad \begin{matrix} h=1,2,\ldots,f \\ \ell=1,2,\ldots,f \end{matrix}$$

and

$$(6.5) \qquad g_h = -\sum_j \left[\left(\frac{r_{hj}}{x_j} - \frac{\sum_{i \epsilon \langle [j] \rangle} r_{hi}}{\sigma_{[j]}} \right) u_j \right] . \qquad h=1,2,\ldots,f$$

We may then solve Eq. (6.3) for $\alpha_1, \alpha_2, \ldots, \alpha_f$, and substitute these values into Eq. (6.2) to get the rates.

In using this method, one must start with the fast reactions in equilibrium. Indeed, the only way the equilibrium constants of the fast reactions are known to the integration routine are via the initial values of the substances entering into the equilibrium reaction. Since the concentrations of the substances in the fast reactions are in the denominator of Eq. (5.6), the initial concentration of any substance entering into a fast reaction may not be zero. However, it is permissible to start with extremely small amounts, less than trace quantities, of the substance entering into the fast reactions. This will not cause undue roundoff errors when using floating-point arithmetic. To summarize, the derivatives are evaluated as follows:

a) The contributions, u_j, of the slow reactions are calculated using Eq. (6.1);

b) The coefficients for the simultaneous equations are calculated using Eq. (6.4) and Eq. (6.5);

c) The simultaneous equations (6.3) are solved for $\alpha_1, \alpha_2, \ldots, \alpha_f$;

d) And finally, $\alpha_1, \alpha_2, \ldots, \alpha_f$ are substituted into Eq. (6.2) to get the rates of change of the variables.

A simplification in the above may be made by assuming that $\dot{\sigma}_k = 0$ for all phases k. Then Eq. (5.7) becomes

$$\frac{\dot{\hat{x}}_i}{\hat{x}_i} \quad \frac{\dot{c}_i}{c_i} = \frac{\dot{x}_i}{x_i} ,$$

and the term

$$\frac{\sum_{i \epsilon \langle [j] \rangle} r_{hi}}{\sigma_{[j]}}$$

drops out of Eq. (6.4) and Eq. (6.5).

7. The Conservation Equations

For the quantities appearing in Eqs. (6.1), define

$$(7.1) \qquad q_{\ell j} = n_{\ell j} - m_{\ell j}$$

$$(7.2) \qquad g_\ell = f_\ell \left(k_\ell \prod_{i=1}^{N} \hat{x}_i^{m_{\ell i}} - k'_\ell \prod_{i=1}^{N} \hat{x}_i^{n_{\ell i}} \right) .$$

Then Eq. (6.2) may be written as

$$(7.3) \qquad \dot{x}_j = \sum_{\ell=1}^{s} g_\ell q_{\ell j} + \sum_{\ell=1}^{f} \alpha_\ell r_{\ell j} \ .$$

Define vectors:

$$\dot{x} = \begin{pmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \vdots \\ \dot{x}_N \end{pmatrix} \qquad g = \begin{pmatrix} g_1 \\ g_2 \\ \vdots \\ g_s \end{pmatrix} \qquad \alpha = \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_f \end{pmatrix}$$

and matrices

$$Q = (q_{\ell j}) \qquad \begin{matrix} \ell=1,2,\ldots,s \\ j=1,2,\ldots,N \end{matrix}$$

$$R = (r_{\ell j}) \qquad \begin{matrix} \ell=1,2,\ldots,f \\ j=1,2,\ldots,N \end{matrix}$$

Then Eq. (7.3) becomes

$$(7.4) \qquad \dot{x} = Q^T g + R^T \alpha$$

Let S be a matrix of maximal rank and of full row rank such that

(7.5) $$SQ^T = 0 \ ,$$

and

(7.6) $$SR^T = 0 \ ,$$

letting M = rank(S), S is an M×N matrix. Then

(7.7) $$\dot{Sx} = S(Q^T g + R^T \alpha) = 0$$

by Eqs. (7.4) through (7.6). Since R and Q are independent of time, it follows that S is also; letting

$$b = Sx_1$$

where x_1 is x evaluated at any time, we have

(7.8) $$Sx = b \text{(constant vector)}$$

at all times. The M linear relationships given by Eq. (7.8) are the conservation equations that the system (7.4) must obey. It also follows that

$$M = N - f - s$$

if the f + s rows in Q and R are linearly independent.

The conservation equations are useful as an accuracy check when integrating the kinetic Eqs. (7.4).

8. An Algorithm for Finding the Conservation Equations

For purposes of the algorithms to be described, combine the Q and R matrix of the previous section into a single matrix whose number of rows is f + s. Denote this new matrix, for the purpose of the algorithm, as R, and let R be an M'xN matrix. Normally, the M' rows of R will be linearly independent, but this is not absolutely necessary, as the algorithm below will indicate when a row is linearly dependent on other rows. In any event, if a row is known to be linearly dependent on other rows, it should be dropped as this simplifies the computations. The algorithm bears a resemblance to the pivoting done in the standard form of the simplex method when solving linear programming problems. However, no reference is necessary to linear programming methods; a "pivot" is here defined to be that linear transformation on a matrix that renders a particular column of that matrix to be a unit vector.

In particular, a pivot on (i_1,j_1) transforms the j_1^{th} column to a unit vector with one in row i_1. The precise operations done in pivoting on (i_1,j_1) are the following:

1) The entry $r_{i_1j_1}$ must be non-zero. Divide every entry in row i_1 by $r_{i_1j_1}$. In particular, $r_{i_1j_1}$ becomes 1.
2) Replace every entry (r_{ij}) not in row i_1 nor column j_1 by $r_{ij} - r_{i_1j} r_{ij_1}$.
3) Replace every entry in column j_1, except for the entry in row i_1, by 0.

The first step in the algorithm is to transform the R matrix to a form where the transformed R matrix has M' columns which are independent unit vectors. It is also desirable to minimize the number of entries of R that are changed from zero entries to non-zero entries. This first step is not unique, since many combinations of M' columns form a linearly independent set (called a <u>basis</u> in linear programming), but some sets are "nicer" than others in the sense that they generate fewer non-zero entries. An algorithm that attempts to do this follows.

Let I(1),I(2),...,I(M') be initially zero. These quantities are the pivot column indicators, and if $I(i_1) = j_1 \neq 0$, this indicates that a pivot was done in (i_1,j_1). Set n = 1, and e = 0.

A) Set J = 1.

B) If any I(i) is equal to J, go to step F. Otherwise continue to step C.

C) Count the number of non-zero entries in column J of R. If this number does not exceed n, go to step D. Otherwise, go to step F.

D) For each non-zero entry (i,J) of column J, check I(i). If no I(i) is found such that I(i) = 0, go to step F. If a non-zero entry is found such that I(i) = 0, pivot on (i,J) and set I(i) = J, and go to step E.

E) Increase e by 1. If e = M' terminate the algorithm.

F) Increase J by 1. If J ≤ N go to step B. Otherwise, go to step G.

G) Increase n by 1. If n ≤ M' go to step A. Otherwise terminate the algorithm.

When this algorithm terminates, every row i that has been pivoted in will be indicated by having $I(i) \neq 0$. If $I(i) = 0$, then row i is linearly dependent on the other rows, and it may be dropped from further consideration.

Each column of R that has not been pivoted in is now used to form the coefficients of a row of the conservation matrix. Suppose the j^{th} column of R was not pivoted in. Let $s_1, s_2, \ldots, s_N$ be the coefficients of the corresponding row of the conservation matrix. Begin with $s_1 = s_2 = \ldots = s_N = 0$. Set $s_j = 1$. Then set $s_{I(i)} = -r_{ij}$ for $i=1,\ldots,M'$. $s_1, s_2, \ldots, s_N$ are now set to their correct values.

The matrix representation of this method is as follows:

Let R_1 be a square submatrix of R such that R_1 is invertable and $R = [R_1\ R_2]$. Then the conservation matrix as

constructed above is

$$S = \left(-R_2^T (R_1^T)^{-1} \quad I \right).$$

It is easily seen that $SR^T = 0$.

Example:

Using the two-phase system given in Sec. 2, let the reactions be:

$$H_2(\text{gas}) \rightleftharpoons H_2(\text{liquid})$$

$$O_2(\text{gas}) \rightleftharpoons O_2(\text{liquid})$$

$$2H_2(\text{gas}) + O_2(\text{gas}) \rightleftharpoons 2H_2O(\text{gas})$$

$$2H_2(\text{liquid}^*) + O_2(\text{liquid}^*) \rightleftharpoons 2H_2O(\text{liquid})$$

The coefficient matrix of this system is:

	Gas Phase			Liquid Phase		
	H_2	O_2	H_2O	H_2	O_2	H_2O
Reaction 1	1	0	0	-1	0	0
Reaction 2	0	1	0	0	-1	0
Reaction 3	2	1	-2	0	0	0
Reaction 4	0	0	0	2	1	-2
Column	1	2	3	4	5	6

NOTE: that the reaction $H_2O(\text{gas}) \rightleftharpoons H_2O(\text{liquid})$ although it may be the most important, has been dropped, since it is redundant.

*Dissolved in the liquid phase.

By choosing columns 1, 2, 3, and 6 to pivot in, one obtains,

I(1) = 1	(1)	0	0	-1	0	0
I(2) = 2	0	(1)	0	0	-1	0
I(3) = 3	0	0	(1)	-1	$-\frac{1}{2}$	0
I(4) = 6	0	0	0	-1	$-\frac{1}{2}$	(1)

Since columns 4 and 5 were not pivoted in, the conservation matrix has an identity matrix in two columns 4 and 5, and the conservation matrix becomes:

Gas			Liquid		
H_2	O_2	H_2O	H_2	O_2	H_2O
1	0	1	1	0	1
0	1	$\frac{1}{2}$	0	1	$\frac{1}{2}$

Here the first row of the conservation matrix represents the conservation of H_2 and the second row represents the conservation of O_2.

9. The Differential System in Matrix Notation

In order to write Eqs. (6.2) through (6.5) in matrix notation, define the following matrices:

$$R = (r_{\ell j}) \qquad \begin{matrix} \ell=1,2,\ldots,f \\ j=1,2,\ldots,N \end{matrix}$$

$$V = (v_{i\ell}) \qquad \begin{matrix} i=1,2,\ldots,f \\ \ell=1,2,\ldots,f \end{matrix}$$

and the following vectors:

$$x = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \end{pmatrix} \qquad \dot{x} = \begin{pmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \vdots \\ \dot{x}_N \end{pmatrix} \qquad u = \begin{pmatrix} u_1 \\ u_2 \\ \vdots \\ u_N \end{pmatrix} \qquad \alpha = \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_f \end{pmatrix}$$

$$\hat{x} = \begin{pmatrix} \hat{x}_1 \\ \hat{x}_2 \\ \vdots \\ \hat{x}_N \end{pmatrix} \qquad \sigma = \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \vdots \\ \sigma_p \end{pmatrix}$$

and others when needed, by analogy. Defining the diagonal matrices

$$X = \text{diag } (x)$$

$$\hat{X} = \text{diag } (\hat{x})$$

and the "phase selector" matrix, B, where B is a pxN matrix, such that

$$b_{kj} = \left\{ \begin{array}{lll} 1 & \text{if} & j\epsilon<k> \\ 0 & \text{if} & j\notin<k> \end{array} \right\} \qquad \begin{array}{l} k=1,2,\ldots,p \\ j=1,2,\ldots,N \end{array}$$

Eqs. (5.6) and (5.7) may be written as

$$R\hat{X}^{-1}x = 0 \tag{9.1}$$

and

$$\hat{X}^{-1}\dot{x} = X^{-1}\dot{x} - S^{-1}\dot{s} \tag{9.2}$$

where

$$s = B^{T}\sigma \tag{9.3}$$

$$\dot{s} = B^{T}\dot{\sigma} \tag{9.4}$$

$$S = \text{diag}(s) \tag{9.5}$$

$$\sigma = Bx \tag{9.6}$$

(9.7) $\dot{\sigma} = B\dot{x}$.

Equations (6.2) and (6.3) become

(9.8) $\dot{x} = u + R^T\alpha$

(9.9) $V\alpha = g$.

V and g are determined by substituting Eq. (9.8) into Eq. (9.1) and Using Eqs. (9.2) through (9.7) to eliminate terms involving $\hat{x}$:

(9.10) $R(X^{-1} - S^{-1}B^TB)(u + R^T\alpha) = 0$

and letting

(9.11) $\Omega = X^{-1} - S^{-1}B^TB$

yields

(9.12) $R\Omega R^T\alpha = - R\Omega u$

so that

(9.13) $\quad V = R\Omega R^T$

and

(9.14) $\quad g = R\Omega u$.

If the N substances are ordered so that substances belonging to the same phase have bunched subscripts, then the matrix is partitionable to the form

$$\Omega = \begin{bmatrix} \Omega_1 & 0 & \ldots 0 \\ 0 & \Omega_2 & \ldots 0 \\ \vdots & \vdots & \ddots \\ 0 & 0 \ldots & \Omega_p \end{bmatrix}$$

where each Ω_k is a square matrix whose dimension is the number of substances in phase k. If the substances in phase k are $A_1, A_2, \ldots, A_d$, then Ω_k is of dimension d. The i^{th} diagonal term is

$$\frac{1}{x_i} - \frac{1}{\sigma_k}$$

and all off-diagonal terms are

$$- \frac{1}{\sigma_k} ,$$

where $\sigma_k = \sum_{i=1}^{d} x_i$, and the x_i terms and hence σ_k are positive by consequence of their physical nature.

Definition: A symmetric matrix, M, is positive semi-definite if for every (compatible) vector π,

$$\pi^T M \pi \geq 0 .$$

Also, a matrix, M, is of nullity n if there exist n linearly independent vectors, $\pi_1, \pi_2, \ldots, \pi_n$, but not n + 1 linearly independent vectors such that $M\pi_i = 0$ for i=1,2,...,n.

THEOREM

Each matrix Ω_k, above, is positive semidefinite and of nullity one.

Proof: Let π be any d-vector, $\mathrm{col}(\pi_1 \pi_2 \ldots \pi_d)$. Then

$$\pi^T \Omega_k \pi = \sum_{i=1}^{d} \frac{\pi_i^2}{x_i} - \sum_{i=1}^{d} \sum_{j=1}^{d} \frac{\pi_i \pi_j}{\sigma_k}$$

$$= \sum_{i=1}^{d} \frac{\pi_i^2}{x_i} - \frac{1}{\sigma_k} \left(\sum_{i=1}^{d} \pi_i \right)^2 \qquad (9.15)$$

$$= \sum_{i=1}^{d} \frac{\pi_i^2}{x_i} - \frac{\left(\sum_{i=1}^{d} \pi_i \right)^2}{\sum_{i=1}^{d} x_i} .$$

It is shown elsewhere*, that expressions of the form 9.15 are non-negative (hence the above matrix is positive semidefinite) and are zero if and only if there exists a constant K such that

$$\pi_i = Kx_i$$

for i=1,2,...,d. Since $\Omega_k \pi$ is zero only if $\pi^T \Omega_k \pi$ is zero, Ω_k is of nullity at most one. That the matrix is of nullity one is easily seen by performing the above multiplication, or by noting that Ω_k is singular.

It now follows that Ω is positive semidefinite and of nullity p, and V is also positive semidefinite. If θ is a vector such that $\Omega\,\theta = 0$, then θ is a vector proportional to x in each phase, that is, $\Omega\,\theta = 0$ if and only if θ is of the form $\theta = XB^T\alpha$. As a result of this,

$$\Omega\, XB^T = 0 \ .$$

Note that in order that V be invertable, V must be positive definite [3]. Let A be the conservation matrix associated

*See Ref. 2, p. 72.

with R, that is, A is a matrix of maximal rank such that $AR^T = 0$.

THEOREM

V is singular if and only if the matrix AXB^T is not of full column rank.

Proof: Suppose V is singular. Then there exists a non-zero vector π such that $V\pi = 0$. Thus

$$R\Omega R^T\pi = 0 \ ,$$

hence

$$\pi^T R\Omega R^T\pi = 0$$

or

$$(R^T\pi)^T \Omega (R^T\pi) = 0 \ .$$

By the semidefiniteness of Ω ,

$$\Omega R^T\pi = 0 \ .$$

From the discussion in the above Theorem, there exists a vector α such that

$$R^T\pi = XB^T\alpha$$

and multiplying by A:

$$0 = AR^T\pi = AXB^T\alpha$$

hence, since $\pi \neq 0$ and R is assumed of full rank--hence $R^T\pi \neq 0$ and $\alpha \neq 0$--the matrix AXB^T is not of full column rank. Conversely, assume AXB^T is not of full column rank. Then there exists $\alpha \neq 0$, such that $AXB^T\alpha = 0$. Since R bears the same relationship to A that A bears to R, that is, they are mutually orthogonal and the sum of their row ranks equals the number of their columns, $AXB^T\alpha = 0$ implies that there exists a vector $\pi \neq 0$ such that

$$R^T\pi = XB^T\alpha \ .$$

Multiplying on the left by R

$$V\pi = R\,R^T\pi = R(XB^T)\alpha = 0 \ ,$$

hence V is singular. This completes the proof.

Corollary: If the system to which R corresponds contains only intraphase reactions, then V is invertable.

Corollary: If the system is a single phase (homogeneous) system, then V is invertable.

10. Kinetic Equilibrium

Suppose M' relations of the form of Eq. (5.5) are given:

$$\prod_{i=1}^{N} \hat{x}_i^{r_{\ell i}} = h_\ell \,. \qquad \ell=1,2,\ldots,M' \tag{10.1}$$

Taking logarithms of both sides,

$$\sum_{i=1}^{N} r_{\ell i} \log \hat{x}_i = \log h_\ell \qquad \ell=1,2,\ldots,M' \tag{10.2}$$

and defining vectors

$$\log \hat{x} = \begin{pmatrix} \log \hat{x}_1 \\ \log \hat{x}_2 \\ \vdots \\ \log \hat{x}_N \end{pmatrix} \qquad \log h = \begin{pmatrix} \log h_1 \\ \log h_2 \\ \vdots \\ \log h_N \end{pmatrix}$$

results in the matrix equation:

$$R \log \hat{x} = \log h \quad . \tag{10.3}$$

Let A be the conservation matrix associated with R, and let

$$Ax = b \tag{10.4}$$

be the conservation equations associated with R and the initial values of x, as described in Sec. 7. Assume that rank(R) = M'. Then rank(A) = N - rank(R) = N - M' = M. The problem of finding a non-negative solution to the N non-linear simultaneous equations given by Eqs. (10.3) and (10.4) is designated here as the kinetic equilibrium problem.

Let c be any N-vector such that

$$Rc = - \log h \quad .$$

Several ways of calculating c can be designated, for example, if as in Sec. 8,

$$R = (R_1 \; R_2)$$

with R_1 invertable, c may be partitioned in the same fashion:

$$c = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

and then

$$c_1 = - R_1^{-1} \log h$$

$$c_2 = 0 \ .$$

This calculation has the advantage that a large number of the c_j are zero, but it has the disadvantage that the values are not unique. A unique vector c may be found by noting that there is exactly one c which is orthogonal to A, that is with $Ac = 0$. This vector is

$$c = - R^T(RR^T)^{-1} \log h \ . \tag{10.5}$$

With c determined, Eq. (10.3) may be rewritten:

$$R(c + \log \hat{x}) = 0 \ . \tag{10.6}$$

Since $c + \log \hat{x}$ is orthogonal to R, $c + \log \hat{x}$ is a linear combination of the rows of A: there exists a vector π such that

$$A^T\pi = c + \log \hat{x} \tag{10.7}$$

Equations (10.4) and (10.7) represent N + M equations in the N unknowns x and the M unknowns π. Let L be the following function of x and π:

$$L = x^T(c + \log \hat{x}) - (Ax - b)^T\pi$$

Then [2,4]

$$\frac{\partial L}{\partial \pi} = Ax - b$$

$$\frac{\partial L}{\partial x} = c + \log \hat{x} - A^T\pi$$

Hence Eq. (10.7) is equivalent to

$$\frac{\partial L}{\partial x} = 0 \tag{10.8}$$

and Eq. (10.4) is equivalent to

$$(10.9) \qquad \frac{\partial L}{\partial \pi} = 0 \ .$$

Since

$$(10.10) \qquad F(x) = x^T(c + \log \hat{x})$$

is a convex function [4] of x and Eq. (10.4) is linear in x, the satisfaction of conditions (10.8) and (10.9) represents the minimization of F(x) subject to Eq. (10.4). The chemical equilibrium problem has been known as the problem of finding among the non-negative vectors x that satisfy (10.4) one which minimizes F(x). It is thus evident that

THEOREM

If either the chemical equilibrium problem or the kinetic equilibrium problem has a unique strictly positive solution, then the other problem has the same unique solution.

Thus, in order to find kinetic equilibrium, one may solve the corresponding chemical equilibrium problem.

Example: In the water ionization problem

$$H_2O \rightleftharpoons H^+ + OH^-$$

let $A_3 = H_2O$, $A_1 = H^+$, $A_2 = OH^-$. The equilibrium formula is usually stated in terms of number of moles of solute per liter of water:

$$\text{concentration}(H^+) \times \text{concentration}(OH^-) = 10^{-14} .$$

Assuming that there are $\frac{1000}{18} = 55\frac{5}{9}$ moles of water per liter of water and that the mole fraction of water is very nearly unity, the following equilibrium equation results:

$$\frac{\hat{x}_1\hat{x}_2}{\hat{x}_3} = 10^{-14}\left(\frac{18}{1000}\right)^2 = 3.24 \times 10^{-18} = h_1$$

Hence:

$$\log \hat{x}_1 + \log \hat{x}_2 - \log \hat{x}_3 = -40.27 = \log h_1$$

The conservation equations for this problem are:

$$\begin{aligned} x_1 \quad + x_3 &= b_1 \\ x_2 + x_3 &= b_2 \end{aligned}$$

Using Eq. (10.5) to calculate c with

$$R = [\ 1 \quad 1 \quad -1\ ]$$

$$(RR^T)^{-1} = \left[\frac{1}{3}\right]$$

this results in

$$c = \begin{pmatrix} -\frac{1}{3}\log h_1 \\ -\frac{1}{3}\log h_1 \\ \frac{1}{3}\log h_1 \end{pmatrix} = \begin{pmatrix} 13.76 \\ 13.76 \\ -13.76 \end{pmatrix}$$

11. An Example

The following example of the procedure that might be used to solve a kinetic system includes the various calculations that may be needed for a typical problem. In practice, not all of these calculations would be necessary for every problem.

Defining the Problem. Consider a hypothetical two-phase system, a gas phase and a liquid phase. The gas phase consists of two substances, CO_2 and A, where A

denotes an inert gas (not necessarily Argon). The liquid phase consists of eight substances or species; viz., H_2O CO_2, H^+, OH^-, HCO_3^-, $GgNH_3^+$, $GgNH_2$, and $GgNHCOO^-$. The symbol Gg denotes glycyl-glycine (see [6]). The system has three slow reactions, two of which are intra-phase liquid:

$$\text{(R1)} \qquad H_2O + CO_2 \underset{k_1' = 2{,}855{,}000}{\overset{k_1 = .02}{\rightleftharpoons}} H^+ + HCO_3^-$$

$$\text{(R2)} \qquad CO_2 + GgNH_2 \underset{k_2' = 5{,}737{,}000{,}000}{\overset{k_2 = 88868.8}{\rightleftharpoons}} H^+ + GgNHCOO^- \ ,$$

and one is interphase:

$$\text{(R3)} \qquad CO_2^{(gas)} \underset{k_3' = 100}{\overset{k_3 = 100}{\rightleftharpoons}} CO_2^{(liquid)}$$

and two fast reactions in the liquid phase:

$$\text{(R4)} \qquad H^+ + OH^- \rightleftharpoons H_2O$$

$$\text{(R5)} \qquad H^+ + GgNH_2 \rightleftharpoons GgNH_3^+ \ .$$

The equilibrium constants for the fast reactions are:

$$(E1) \qquad \frac{[H^+][OH^-]}{[H_2O]} = 2.184 \times 10^{-18}$$

$$(E2) \qquad \frac{[H^+][GgNH_2]}{[GgNH_3^+]} = 6.846 \times 10^{-11} \ ,$$

where [ ] denotes mole fraction.*

Finding Conservation Equations of Fast Reactions. First, let us use the method of Sec. 8 to find the conservation equations for the fast reactions only. Figure 1 is a JOSS† program that finds the orthogonal complement S of a matrix R, in accordance with the algorithm of Sec. 8. R is an mxN matrix that is input, and S is the computed MxN matrix. Numbering the above substances

*This example, suggested by Edward C. DeLand, though similar to those in Ref. 6, is not intended to represent a realizable physical system.

†JOSS is the trademark and service mark of The RAND Corporation for its computer program and services using that program. JOSS is a timesharing system used internally at RAND. The program statements are similar to FORTRAN. See Ref. 7 for a description of the JOSS language.

```
1.1 Do step 3 for i=1(1)m.
1.12 Set n=1.
1.14 Set e=0.
1.2 Set J=1.
1.3 Set I(m+1)=J.
1.32 To step 1.6 if first(i=1(1)m+1:I(i)=J)≠m+1.
1.34 Set q=0.
1.36 Do step 3.1 for i=1(1)m.
1.38 To step 1.6 if q>n.
1.4 Set Q=0.
1.42 Do part 4 for i=1(1)m.
1.44 To step 1.6 if Q=0.
1.45 Do part 7 for i=1(1)m.
1.46 Set P(q,J)=1.
1.47 Do part 5 for i=1(1)N.
1.48 Set I(q)=J.
1.5 Set e=e+1.
1.52 To step 1.8 if e=m.
1.6 Set J=J+1.
1.62 To step 1.3 if J≤N.
1.7 Set n=n+1.
1.72 To step 1.2 if n≤m.
1.8 Set M=0.
1.82 Do part 8 for j=1(1)N.

3 Set I(i)=0.
3.1 Set q=q+1 if R(i,J)≠0.
3.2 Set S(M,i)=0.
3.3 Set S(M,I(i))=-R(i,J) if I(i)≠0.

4 Done if I(i)≠0 or |R(i,J)|≤|Q|.
4.1 Set Q=R(i,J).
4.2 Set q=i.

5 Set R(q,j)=R(q,j)/Q.
5.1 Do part 6 for i=1(1)m.

6 Done if i=q.
6.1 Set R(i,j)=R(i,j)-p(i)•R(q,j).

7 Set p(i)=P(i,J).
7.1 Set R(i,J)=0.

8 Set I(m+1)=j.
8.1 Done if first(i=1(1)m+1:I(i)=j)≠m+1.
8.2 Set M=M+1.
8.3 Do step 3.2 for i=1(1)N.
8.4 Set S(M,j)=1.
8.5 Do step 3.3 for i=1(1)m.
```

Figure 1

Number	Component	
1	A	Gas
2	$CO_2^{(gas)}$	phase
3	H_2O	Liquid
4	$CO_2^{(dissolved)}$	phase
5	H^+	
6	OH^-	
7	HCO_3^-	
8	$GgNH_3^+$	
9	$GgNH_2$	
10	$GgNHCOO^-$	

one types:

R(1,5) = 1 R(1,6) = 1 R(1,3) = -1

R(2,5) = 1 R(2,9) = 1 R(2,8) = -1

Let R be sparse.

m = 2

N = 10

Do part 1.

The result (S) of this computation in array form is

$$S = \left[\begin{array}{cc:cccccccc} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hdashline 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{array}\right]$$

From this it is seen that the fast reactions conserve A, CO_2 gas, CO_2 dissolved, HCO_3^-, and $GgNHCOO^-$ (rows 1, 2, 3, 6, and 8), and that the sums

$$H_2O + H^+ + GgNH_3^+$$

$$H_2O + OH^-$$

$$GgNH_3^+ + GgNH_2$$

(rows 4, 5 and 7) are also conserved. Also note that S is decomposable into phases (as indicated by the dashed lines) since there are no interphase fast reactions, and that the components that do not appear in any fast reaction are individually conserved.

Now, suppose the initial quantities of the components of this system are given as follows (in moles):

	Quantity in Moles
Gas	
A	4.00
CO_2	4.8×10^{-5}
Liquid	
H_2O	.25
CO_2	0
H^+	0
OH^-	0
HCO_3^-	0
$GgNH_3^+$	0
$GgNH_2$	1.32×10^{-4}
$GgNHCOO^-$	0

(These values are reproduced in Table 1 in the column headed by 0-.) Then the conservation equations, with respect to the fast reactions are

$$Sx = b$$

where

$$b = Sx_o$$

Table 1

Component		Time (see text)			
		0-	0+	5.2 sec	∞
Gas Phase	A	4	4	4	4
	CO_2	4.8×10^{-5}	4.8×10^{-5}	1.097×10^{-5}	2.81×10^{-6}
Liquid Phase	H_2O	.25	.249999	.25	.24997
	CO_2	0	0	6.86×10^{-7}	1.75×10^{-7}
	H^+	0	1.34×10^{-13}	1.74×10^{-11}	1.10×10^{-11}
	OH^-	0	1.02×10^{-6}	1.13×10^{-8}	1.24×10^{-8}
	HCO_3^-	0	0	8.40×10^{-8}	2.78×10^{-5}
	$GgNH_3^+$	0	1.02×10^{-6}	3.64×10^{-5}	4.50×10^{-5}
	$GgNH_2$	1.32×10^{-4}	1.3098×10^{-4}	5.94×10^{-5}	6.98×10^{-5}
	$GgNHCOO^-$	0	0	3.63×10^{-5}	1.71×10^{-5}

is evaluated by substituting the above values for x_o:

$$b_1 = 4.00$$
$$b_2 = 4.8 \times 10^{-5}$$
$$b_3 = 0$$
$$b_4 = .25$$
$$b_5 = .25$$
$$b_6 = 0$$
$$b_7 = 1.32 \times 10^{-4}$$
$$b_8 = 0$$

Finding Objective Coefficient for the Chemical Equilibrium Problem Corresponding to the Fast Reactions. In order to get the initial conditions for the kinetic equations, it is necessary to solve

$$Sx = b$$

and (E1-E2) simultaneously for x. For such a simple problem, it is possible to do this manually; however, in larger problems it would be very difficult to solve this problem without the assistance of a computer. The problem may be solved as a chemical equilibrium problem if we

calculate the objective coefficients (c) as described in Sec. 10. Figure 2 (a continuation of the JOSS program of Fig. 1) calculates $c_1,\ldots,c_{10}$ from the results of the calculations in Fig. 1. This is done by inputting the negative logarithms of the equilibrium constants of E1 and E2 and giving the execute instruction, as follows:

$$h(1) = -\log (2.184 \times 10^{-18})$$

$$h(2) = -\log (6.846 \times 10^{-11})$$

Do part 11.

This results in

$$c(1) = c(2) = c(3) = c(4) = c(5) = c(7) = c(8) = c(10) = 0$$
$$c(6) = 40.665$$
$$c(9) = 23.405 .$$

Solving the Chemical Equilibrium Problem Corresponding to the Fast Reactions. The next step would be to solve a chemical equilibrium problem: minimize Eq. (10.10) subject to Eq. (10.4) using S for A. In order to use the methods of Ref. 2 to solve this problem, it is necessary to eliminate

```
11    Do part 13 for j = 1 (1) N.

11.1  Do part 12 for i = 1 (1) m.

12.1  Set c(T(i)) = sum(j = 1 (1) m: R(i, I(j)) • h(j)).

13.1  Set c(j) = 0.
```

Figure 2

the substances that have zero initial quantities and enter into no fast reactions. Hence CO_2 (liquid), HCO_3, and $GgNHCOO^-$ should be eliminated. In addition, the non-participating gas phase may be eliminated. If these eliminations are made, it is seen that rows 1, 2, 3, 6, and 8 of the S (now A) matrix are null, and these rows should be eliminated. This results in the system:

$$A = \begin{array}{c} \begin{matrix} H_2O & H^+ & OH^- & GgNH_3^+ & GgNH_2 \end{matrix} \\ \begin{bmatrix} 1 & 1 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 \end{bmatrix} \end{array} \qquad B = \begin{bmatrix} .25 \\ .25 \\ 1.32 \times 10^{-4} \end{bmatrix}$$

$$C = \begin{bmatrix} 0 & 0 & 40.665 & 0 & 23.405 \end{bmatrix}$$

Solving this chemical equilibrium problem results in:

	Quantity Moles
H_2O	.24999
H^+	1.34×10^{-13}
OH^-	1.02×10^{-6}
$GgNH_3^+$	1.02×10^{-6}
$GgNH_2$	1.3098×10^{-4}

(These values are shown in Table 1 in column headed by 0+.) The mole fractions of each of these quantities are approximately four times the above: these may be checked to see that they approximately satisfy E1 and E2.

Integrating the Kinetic Equations. The final step would be to input these values, together with the original values for the gas phase into a routine that integrates the kinetic equations. We used a SHARE program [8] to integrate the differential equations (Eq. (6.2)). This program uses a variable step size Adams-Moulton scheme in order to minimize round-off error. The integration program calls a SUBROUTINE DAUX which evaluates the right sides of Eq. (6.2). (The subroutine, written by Rose Heirschfeldt of RAND, is reproduced in the Appendix.) The integration of the differential equations is especially sensitive to the values of certain parameters, denoted by $\bar{E}$ and A, required by the program. The program calculates for each variable x_i, a predicted value, $y_i^{(p)}$, and a corrected value, $y_i^{(c)}$. The fractional error in x_i is taken to be

$$E_i = \frac{|y_i^{(p)} - y_i^{(c)}|}{\max(|y_i^{(c)}|, A)} .$$

Then the step size for integration is decreased if any E_i exceeds $\bar{E}$. Hence, $\bar{E}$ is the maximum fractional error in x_i subject to the denominator in the calculation of E_i being no less than A. In the above test problem (run on an IBM 7044) it was found that satisfactory results were obtained if

$$\bar{E} = 10^{-4}$$

$$A = 10^{-6}$$

Unity was used for f_ℓ (Eq. (1.4)) for the fast reactions. The results of the first 5.2 seconds of reaction time (for certain of the quantities) are shown in Fig. 3. H_2O and A were approximately constant and H^+ was off the graph at the bottom. Note that the first 0.1 sec for $CO_2^{(liquid)}$ and $GgNHCOO^-$ are not shown since they begin at zero and quickly move to the curves shown.

Finding the Conservation Equations for All of the Reactions. After the kinetic equations have been integrated, the values obtained at various times may be checked against the conservation equations of all of the reactions in order to determine the amount of roundoff error present.

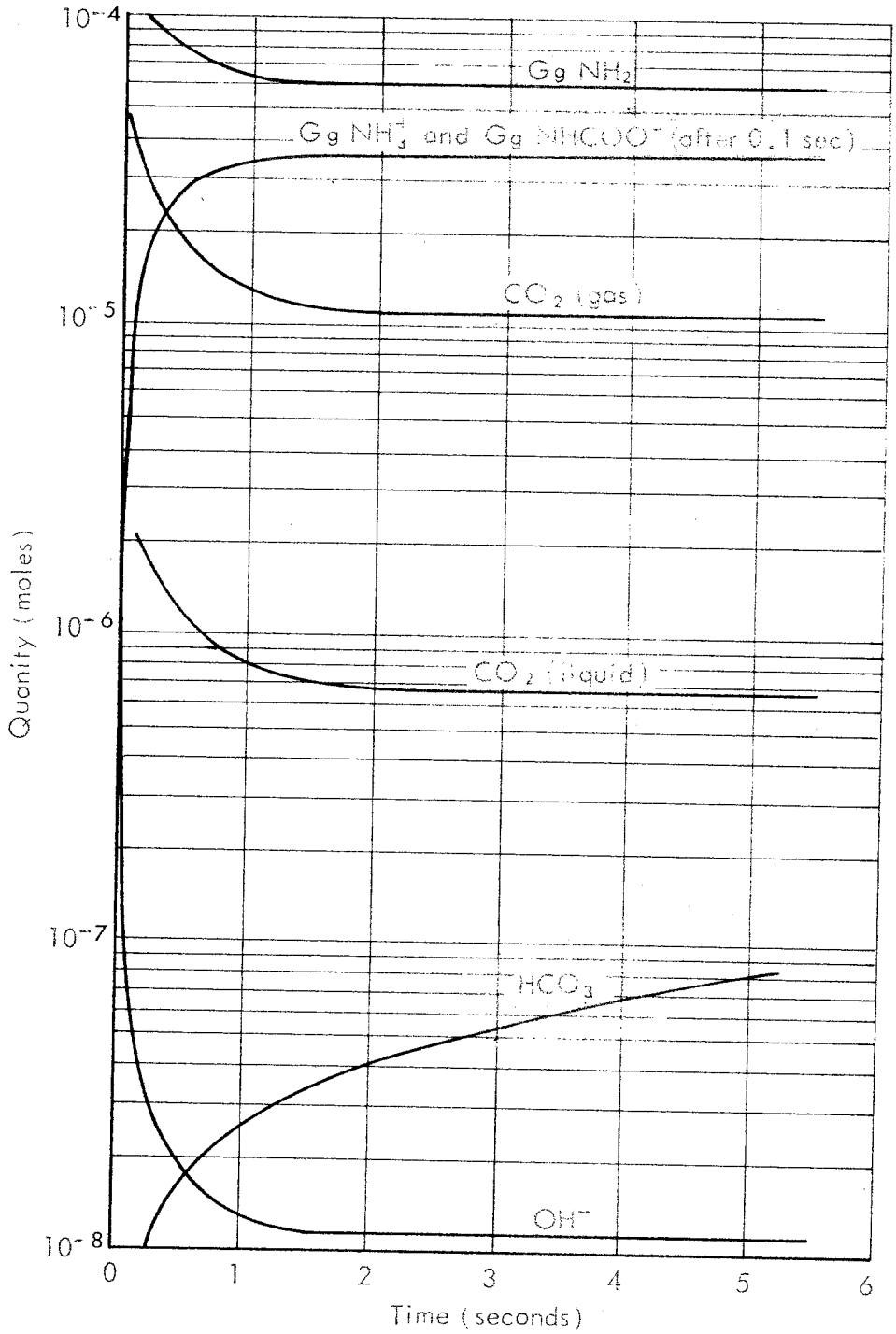
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
Quanity (moles)
$G_g NH_2$
$G_g NH_3^+$ and $G_g NHCOO^-$ (after 0.1 sec)
CO_2 (gas)
CO_2 (liquid)
HCO_3^-
OH^-
0
1
2
3
4
5
6
Time (seconds)

Figure 3

The conservation equations for all of the reactions are found in the same way that the conservation equations were found for the fast reactions only. The R matrix is

$$R = \begin{bmatrix} 0 & 0 & 1 & 1 & -1 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 1 & -1 \\ 0 & 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & -1 & 1 & 0 \end{bmatrix}$$

The conservation matrix associated with these reactions as found by the method of Fig. 1 is

$$S = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 1 & 0 & -1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & -1 & -2 \\ 0 & 0 & 1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 \end{bmatrix}$$

The columns of S that are unit vectors--those representing the substances A, CO_2, H^+, HCO_3^-, and $GgNH_3^+$--are the elementary constituents of the conservation equations associated with this matrix. A linear transformation may be performed on the conservation matrix without altering its validity; in order to replace HCO_3^- and $GgNH_3^+$ by OH^-

and $GgNH_2$ as elementary constituents, add the fourth row to the second row and add the fifth row to the third row. Doing this, and changing the name of S to A to conform with Sec. 10--

$$A = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 \end{bmatrix}$$

--to obtain b for the conservation equations, substitute the first column of Table 1 into

$$b = Ax_o \ ,$$

obtaining

$$b(1) = 4$$

$$b(2) = 4.8 \times 10^{-5}$$

$$b(3) = .25$$

$$b(4) = .25$$

$$b(5) = 1.32 \times 10^{-4} \ .$$

To get the objective coefficients for the corresponding chemical equilibrium problem, continue the computation of Fig. 1 with that of Fig. 2, letting

$$h(1) = -\log (2855000/.02)$$
$$h(2) = -\log (5.737 \times 10^{9}/88868.8)$$
$$h(3) = -\log (100/100)$$
$$h(4) = -\log (2.184 \times 10^{-18})$$
$$h(5) = -\log (6.846 \times 10^{-11}) \ .$$

This results in

$$c(3) = -18.7766054$$
$$c(6) = 21.8887682$$
$$c(9) = 34.4800574$$
$$c(1) = c(2) = c(4) = c(5) = c(7) = c(8) = 0 \ .$$

Solving this two-phase chemical equilibrium problem gives the results in the column of Table 1 headed by ∞. The results of the kinetic program at the end of 5.2 sec are also given in Table 1. These values are seen to very nearly satisfy the conservation equations.

Thus, one check for the accuracy of the kinetic program was effected; although incorrect results are possible even though conservation equations are satisfied. Note also (from Fig. 3 and Table 1) that the convergence of this example is very slow--primarily because of the small forward rate (.02) of the first slow reaction. It is possible to speed up the computation of the reactions in this example by changing (after a few seconds of reaction time) R2 and R3 to be fast reactions. This would leave R1 as the only slow reaction, and R3 would be an interphase fast reaction.

Appendix

THE AUXILLIARY DERIVATIVE SUBROUTINE

This Appendix presents the subroutine that calculates the derivatives used in integrating the kinetic equations. There are two "CALLS" made by the subroutine which do the following:

1) BAR calculates σ_k (as in Eq. (2.1)) and stores it in XBAR(k);

2) CHOL solves the simultaneous equations (Eq. (6.3)) and stores the result in the vector G.

The common storage contains an array T (described in Ref. 8). Some of the symbols in the common storage are not used in the subroutine, and should be ignored. The relevant symbols follow, together with their values for the example of Sec. 11.

Symbol and Example Value	Meaning
N = 10	Number of substances.
NCOMP = 2	Number of compartments.
NFAST = 2	Number of fast reactions.
NSLOW = 3	Number of slow reactions.
KLA(1) = 1 KLA(2) = 3	KLA(K) is the sequence number of the first substance in compartment K.

Symbol and Example Value	Meaning
KLB(1) = 2 KLB(2) = 10	Sequence number of last substance in compartment.
CS(1) = .02 CS(2) = 868868.8 CS(3) = 100	CS(ℓ) is the forward reaction rate for slow reaction ℓ.
CT(1) = 2.855×10^6 CT(2) = 5.737×10^9 CT(3) = 100	Backward reaction rate.
KCF(1) = 2 KCF(2) = 2 KCF(3) = 0	The compartment that the slow reaction is in. KCF is zero for an interphase reaction.
NAS(1) = 1 NAS(2) = 3 NAS(3) = 5	NAS refers to the NS and AS lists below. NAS(ℓ) is the subscript of the first entry in the NS and AS lists that pertains to reaction ℓ.
NBS(1) = 2 NBS(2) = 4 NBS(3) = 5	NBS(ℓ) is the last subscript of the NS and AS lists that refers to reaction ℓ
AS(1) = 1 AS(2) = 1 AS(3) = 1 AS(4) = 1 AS(5) = 1	AS(j) is the <u>forward</u> coefficient for substance NS(j) in the <u>slow</u> reaction ℓ for which j is between NAS(ℓ) and NBS(ℓ). Hence AS(1) and AS(2) refer to slow reaction 1 and since NS(1) is 3 and NS(2) is 4, this means that the coefficient for the forward reaction for the third and fourth substances (which are H_2O and H^+) are 1. If a substance is not given for a particular reaction, its coefficient is zero.
NS(1) = 3 NS(2) = 4 NS(3) = 4 NS(4) = 9 NS(5) = 2	

Symbol and Example Value	Meaning
NAT(1) = 1 NAT(2) = 3 NAT(3) = 5 NBT(1) = 2 NBT(2) = 4 NBT(3) = 5 AT(1) = 1 AT(2) = 1 AT(3) = 1 AT(4) = 1 AT(5) = 1 NT(1) = 5 NT(2) = 7 NT(3) = 5 NT(4) = 10 NT(5) = 4	NAT, NBT, AT, and NT are respectively the same as NAS, NBS, AS, and NS, except that these refer to the backward coefficients (as opposed to the forward coefficients for the latter) of the slow reactions.
NAF(1) = 1 NAF(2) = 4 NBF(1) = 3 NBF(2) = 6 AF(1) = -1 AF(2) = 1 AF(3) = 1 AF(4) = 1 AF(5) = -1 AF(6) = 1 NF(1) = 3 NF(2) = 5 NF(3) = 6 NF(4) = 5 NF(5) = 8 NF(6) = 9	NAF, NBF, AF, NF are similar to NAT, NBT, AT, NT, except that these refer to the fast reactions. Forward and backward coefficients are distinguished by using a minus sign for the backward coefficients.

Symbol and Example Value	Meaning
R(1,1) = 0 R(1,2) = 1 R(2,1) = 0 R(2,2) = 1	R(h,K) is the value of the expression $\sum_{i \in \langle K \rangle} r_{hi}$ mentioned at the end of Sec. 6, where h runs over the fast reactions and K over the compartments.

```
      SUBROUTINE DAUX
      COMMON KA(18),KN(100,2),NAM(10,4),KLA(10),KLB(10),Y(100),
     1 NRS(50,3),NRF(50,3),CS(50),CT(50),KCF(50),AS(200),NS(200),
     2          NAS(50),NAT(50),NAF(50),          AT(200),NT(200),
     3          NBS(50),NBT(50),NBF(50),          AF(200),NF(200),
     4 XBAR(10),XMF(100),N,NCOMP,NFAST,NSLOW,END,BLANK
      INTEGER END,BLANK
      COMMON CF(50),NIT,NOT/MS/LIMIT /DUX/T(1003)
      COMMON/DRV/V(50,50),G(50)
      COMMON/EXPSUM/R(50,10)
      EQUIVALENCE (TIME,T(2)),(DX,T(3)),(X,T(4))
      EQUIVALENCE (G,ALPHA)
      DIMENSION X(100)
      DIMENSION ALPHA(50)
C COMPUTE CONCENTRATIONS
      CALL BAR(X,XBAR)
      DO 10 K=1,NCOMP
      K1=KLA(K)
      K2=KLB(K)
      DO 11 J=K1,K2
      XMF(J)= AMAX1(X(J)/XBAR(K),1.E-30)
      IF(X(J).LT.0.) WRITE(NOT,1000)  J,X(J)
 1000 FORMAT(3H X(I2,4H) = E20.5)
   11 CONTINUE
   10 CONTINUE
C
C PART OF DERIVATIVES CONTRIBUTED BY SLOW REACTIONS
      DO 1 J=1,N
C
C     DERIVATIVES MUST BE STORED FROM T(N+4) FOR INTEGRATION ROUTINE W031
      JJ=J+N+3
      T(JJ)=0.
      DO 2 L=1,NSLOW
      PARX=1.
      KCFA=KCF(L)
      IF(KCFA.NE.0) PARX=XBAR(KCFA)
      PS=1.
      PT=1.
C    FORWARD
      K1=NAS(L)
      K2=NBS(L)
      AMJL=0.
      DO 20 K=K1,K2
      IF(NS(K).EQ.J) AMJL=AS(K)
      I=NS(K)
      PS=PS*XMF(I)**AS(K)
   20 CONTINUE
```

```
C
C    BACKWARD
       K1=NAT(L)
       K2=NBT(L)
       ANJL=C.
       DO 24 K=K1,K2
       IF(NT(K).EQ.J) ANJL=AT(K)
       I=NT(K)
       PT=PT*XMF(I)**AT(K)
    24 CONTINUE
C
       T(JJ)=T(JJ)+BARX * (CS(L)*PS-CT(L)*PT) * (ANJL-AMJL)
     2 CONTINUE

          1 CONTINUE
C
C FAST REACTIONS
C CALCULATE COEFFICIENTS FOR SIMULTANEOUS EQUATIONS
          DO 50 K=1,NFAST
          G(K)=C.
          DO 50 L=1,NFAST
       50 V(K,L)=0.
C
          DO 12 JCOMP=1,NCOMP
          MLA=KLA(JCOMP)
          MLB=KLB(JCOMP)
          DO 5 J=MLA,MLB
          JJ=J+N+3
C
          DO 4 K=1,NFAST
          K1=NAF(K)
          K2=NBF(K)
          DO 52 I=K1,K2
            IF(NF(I).EQ.J) GO TO 54
       52   CONTINUE
          IF(R(K,JCOMP).EQ.C.) GO TO 4
          Q= -R(K,JCOMP)/XBAR(JCOMP)
          GO TO 56
       54 Q=AF(I)/X(J)-R(K,JCOMP)/XBAR(JCOMP)
       56 CONTINUE
          G(K)=G(K) - Q*T(JJ)
C
          DO 3 L=1,NFAST
          K1=NAF(L)
          K2=NBF(L)
           DO 58 I=K1,K2
            IF(NF(I).EQ.J) GO TO 62
       58   CONTINUE
          GO TO 3
       62 V(K,L)=V(K,L)+Q*AF(I)
```

```
C
    3     CONTINUE
    4    CONTINUE
    5   CONTINUE
   12  CONTINUE
C
C   SOLVE SIMULTANEOUS EQUATIONS
       CALL CHOL(V,NFAST,G,-1,CF,ISING,50)
       IF(ISING.EQ.0) GO TO 65
       WRITE(NOT,100)
  100  FORMAT(27HC MATRIX IS SINGULAR - EXIT)
       CALL EXIT
C    ALPHA'S NOW REPLACE G'S
C
C  NOW SUM CONTRIBUTIONS OF FAST REACTIONS
   65  CONTINUE
       DO 8 J=1,N
       JJ=J+N+3
       RA=0.
       DO 7 L=1,NFAST
       K1=NAF(L)
       K2=NBF(L)
       DO 6 K=K1,K2
       IF(NF(K).NE.J) GO TO 6

       RA=RA+AF(K)*ALPHA(L)
       GO TO 7
    6    CONTINUE
    7   CONTINUE
C
C  TOTAL RATES OF CHANGE
       T(JJ)=T(JJ)+RA
    8  CONTINUE
       RETURN
       END
```

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