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Status Report

on

COMPUTATION OF THE EQUILIBRIUM COMPOSITION OF REACTING GAS-SOLID MIXTURES WITH MATERIAL AND ENERGY BALANCE CONSTRAINTS

by

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I. SUMMARY

The computation of chemical equilibrium composition for a multi-component, poly-phase system requires the minimization of the equation which expresses the free energy of the system subject to mass balance constraints. At low temperatures the equilibrium composition of the degradation products of nylon-phenolic resin ablative composites are not in agreement with experimentally determined values. In trying to improve the agreement a new approach is proposed. This consists of solving the minimization problem with an energy balance constraint in addition to the mass balance constraints. Comparing the composition computed from this restricted equilibrium calculation with experimental data showed that there was an order of magnitude agreement with the low molecular weight species present. However, the high molecular weight species that were found to be present experimentally were not predicted to be present by the calculations except in trace amounts.

II. INTRODUCTION

There are several techniques presently available to compute complex chemical equilibrium (1,2,3). One of the most useful is referred to as free energy minimization. This technique takes advantage of the fact that at equilibrium the free energy is a minimum. The usual procedure is to solve the free energy equation subject to material balance constraints. A detailed discussion of this technique was given by del Valle, et.al. (4). In the case of the pyrolysis products of a nylon-phenolic resin ablative composite, the chemical equilibrium composition computed by this method is not in agreement with the experimentally determined values. To try to improve this agreement Swann (5) has suggested that this problem be solved with the addition of an energy balance constraint. The nature of this constraint is explained in detail in this report. The equations resulting from this technique are derived following a procedure similar to the one used by the authors in reference (4). Results of the computer program implementation are presented and compared with experimental compositions for the degradation products of a nylon-phenolic resin ablative composite. The comparison shows an order of magnitude between computed compositions and experimental values of Sykes (6,7) only for the low molecular weight species present. The computer program listing and typical results are given in the Appendix A.

III. THE EQUATIONS FOR RESTRICTED EQUILIBRIUM

A method is proposed in this report where a "restricted equilibrium state" is defined. This equilibrium state is obtained by adding to the regular free energy minimization algorithm an additional constraint, i.e. an energy balance constraint. This constraint adds an additional equation to the free energy minimization technique. The derivation of the equations follows.

Material Balance Constraints:

Consider a mixture containing a number of chemical species (n gaseous and n+1 to q condensed species). The material balance for the number of grams- atoms of element j in the mixture can be written as:

$$\sum_{i=1}^{n} a_{ij}\, x_i + \sum_{i=n+1}^{q} a_{ij}\, x_i = b_j \qquad j = 1, 2, \ldots .m \qquad (1)$$

where m is the total number of elements.

Free Energy Functions:

The free energy expression for each of the n gaseous species can be expressed by the relation for an ideal gas mixture:

$$f_{i,(gas)} = x_i\,(c_i + \ln(x_i/\bar{x}) \qquad i = 1 \ldots . n \qquad (2)$$

where

$$c_i = (\bar{F}^\circ/RT)_i + \ln P \qquad i = 1 \ldots . n \qquad (3)$$

and

$$\bar{x} = \sum_{i=1}^{n} x_i \qquad (4)$$

Assuming the partial pressure of the condensed species to be neglible; the free energy expression for these species becomes

$$f_{i,(solid)} = x_i \left[\bar{F}^\circ_T/RT\right] \qquad i = n+1 \ldots . q \qquad (5)$$

Hence, the total free energy function of the mixture is the sum of Equations (2) and (5). This is expressed as

$$F(X) = \sum_{i=1}^{n} f_{i,(gas)} + \sum_{i=n+1}^{q} f_{i,(solid)}$$

or in the expanded form

$$F(X) = \sum_{i=1}^{n} x_i \left[c_i + \ln (x_i/\bar{x})\right] + \sum_{i=n+1}^{q} x_i \left[\bar{F}^\circ_T/RT\right]_i \tag{6}$$

For a given temperature and pressure it is necessary to determine the amount of each chemical species present, x_i, theat minimizes the free energy function Equation (6). This is subject to the specification of the total amount of each element present, i.e., constant, b_j, of Equation (1). The usual analytical procedure is to form the constrained equation or augmented function and equate the partial derivatives with respect to x_i of this function to zero. However, this procedure results in a set of equations with the x_i's expressed implicitly. To obtain a simplet, but iterative solution, a quadratic approximation fo the free energy function is formed by Taylor series expansion about a specified point $Y(y_1, y_2, y_3 \ldots y_q)$ and neighboring point $X(x_1, x_2, x_3 \ldots x_q)$. The augmented function is then formed using this approximation.

The partial derivatives of this function, with respect to the x_i's are equated to zero. This results in a set of equations with the x_i's expressed explicitly.

The Taylor series expansion to the free energy function of Equation (6), neglecting terms higher than second order, is

$$Q(X) = F(Y) + \sum_{i=1}^{q} \frac{\partial F}{\partial y_i} \Delta_i + \frac{1}{2} \sum_{i=1}^{q} \sum_{k=1}^{q} \frac{\partial^2 F}{\partial y_i \partial y_k} \Delta_i \Delta_k \tag{7}$$

where

$$\Delta_i = x_i - y_i \qquad i = 1 \ldots\ldots q \tag{7a}$$

Taking the appropriate partial derivatives

$$\frac{\partial F(Y)}{\partial y_i} = c_i + \ln(y_i/\bar{y}) \quad \text{(for gases)} \quad i=1\ldots\ldots n \tag{8a}$$

$$\frac{\partial F(Y)}{\partial y_i} = \left[\frac{\bar{F}^o_T}{RT}\right]_i \quad \text{(for condensed species)} \quad i = n+1\ldots q \tag{8b}$$

$$\frac{\partial^2 F(Y)}{\partial y_i \partial y_k} = \frac{\delta_{ik}}{y_i} - \frac{1}{\bar{y}} \tag{9}$$

where δ_{ik} is the Kronecher delta. Note that the second partial derivatives of F(Y) with respect to the y_i's of the condensed species are zero. Substituting Equations (8) and (9) in (7) gives the quadratic approximation to the free energy function at X expanded about Y. Thus,

$$Q(X) = F(Y) + \sum_{i=1}^{n} c_i + \ln(y_i/\bar{y})\ \Delta_i + \frac{1}{2}\sum_{i=1}^{n}\sum_{k=1}^{n}\left(\frac{\delta_{ik}}{y_i} - \frac{1}{\bar{y}}\right)\Delta_i\Delta_k + \sum_{i=n+1}^{q}\left[\frac{\bar{F}^o_T}{RT}\right]_i \Delta_i \tag{10}$$

Heat Balance Constraint:

The heat of pyrolysis of a degrading plastic can be computed using the following equation (8):

$$\Delta H_{pyr} = \sum_{i=1}^{q}\left[x_{p,i}\ \Delta H_{f,i} + \int_{25°C}^{T_p} x_{p,i}\ C_{p,i}\ dT\right] - \sum_{j=1}^{1}\left[x_{r,j}\ \Delta H_{f,j} + \int_{25°C}^{T} x_{r,j}\ C_{p,j}\ dT\right] \tag{11}$$

where q is the total number of species present in the pyrolysis products and 1 is the total components in the ablative composite. For nylon-phenolic resin composites, the temperature, T_r, where the degradation starts is approximately 300°C. and the final temperature is approximately 1000°C. Pyrolysis products are generated over this temperature range and

T_p is the appropriate average temperature which gives the correct energy associated with the pyrolysis products. It was determined to be 700°C as a weighted average based on the mass loss rate (8):

Rearranging Equation (11) gives:

$$\Delta H_{pyr} + \sum_{j=1}^{l} \left[x_{r,j} \, \Delta H_{f,j} + \int_{25°C}^{T_r} x_{r,j} \, C_{p,j} \, dt \right] = - \sum_{j=1}^{q} \left[x_{p,i} \, \Delta H_{f,i} + \int_{25°C}^{T_p} x_{p,i} \, C_{p,i} \, dT \right] \tag{12}$$

The left hand side of Equation (12) is known from experimentally determined values and define b_{j+1} as the left hand side.

$$b_{j+1} = \sum_{i=1}^{q} \left[x_{p,i} \, \Delta H_{fi} + \int_{25°C}^{T_p} x_i \, C_{pi} \, dT \right] \tag{13}$$

Notice that the x_p's are unknown. However, the right hand side of the equation which is unknown, must satisfy the left hand side which is known. Equation (13) can be expanded to the form below, and expanding we have:

$$b_{j+1} = \sum_{i=1}^{n} \left[x_i \, \Delta H_i + \int_{25°C}^{T_p} x_i \, C_{pi} \, dT \right] + \sum_{i=n+1}^{q} \left[x_i \, \Delta H_i + \int_{25°C}^{T_p} x_i \, C_p \, dT \right] \tag{14}$$

Note that Equation (14) has been written in the same form as the material balance equations. This simplifies considerably the final form of the equations to be solved.

In addition, define H_i as:

$$H_i = \Delta H_i + \int_{25°C}^{T_p} C_p \, dT$$

This is done to avoid carrying the integral term in the derivation; and the resulting equation is

$$b_{j+1} = \sum_{i=1}^{n} H_i \, x_i + \sum_{i=n+1}^{q} H_i \, x_i \tag{15}$$

Lagrange Multiplier Formulation and Minimization

To form the augmented function, the quadratic approximation to the free energy, Equation (10) is subjected to the constraints of Equations (1) and (5). Thus, using the method of Lagrange undetermined multipliers, Equation (1) becomes

$$G(X) = Q(X) + \sum_{j=1}^{m} \pi_j \left(b_j - \sum_{i=1}^{q} a_{ij} x_i\right) + \pi_{j+1} \left(b_{j+1} - \sum_{i=1}^{q} x_i \; H_i\right) \tag{16}$$

The condition for equilibrium is $\frac{\partial G(x)}{\partial x_i} = 0$. Hence equation (16) becomes

$$\frac{\partial Q(X)}{\partial x_i} - \sum_{j=1}^{m} \pi_j a_{ij} - \pi_{j+1} \; H_i = 0 \tag{17}$$

But

$$\frac{\partial Q(X)}{\partial x_i} = \left[c_i + \ln \frac{y_i}{\bar{y}}\right] + \left[\frac{x_i}{y_i} - \frac{\bar{x}}{\bar{y}}\right] \qquad i=1...n \tag{18}$$

And

$$\frac{\partial Q(X)}{\partial x_i} = \left[\frac{\bar{\bar{F}}_T^{o}}{RT}\right]_i \qquad i = n + 1 \; ... \; q \tag{19}$$

Substituting (18) in (17), for i = 1,...,n gives

$$\left[c_i + \ln \frac{y_i}{y}\right] + \left[\frac{x_i}{y_i} - \frac{\bar{x}}{y}\right] - \sum_{y=1}^{m} \pi_j a_{ij} - \pi_{j+1} \; H_i = 0 \qquad i = 1...n \tag{20}$$

and (19) into (17), for i = 1,...,q gives

$$\left[\frac{\bar{F}_T^{0}}{R_T}\right]_i - \sum_{j=1}^{m} \pi_j a_{ij} - \pi_{j+1} \; H_i \qquad i = n + 1...q \tag{21}$$

Equation (20) can be solved for x_i (= $x_{i,gas}$) to obtain:

$$x_{i,gas} = -y_i \left[c_i + \frac{y_i}{\bar{y}}\right] + \left[\sum_{j=1}^{m} \pi_j a_{ij} + \pi_{j+1} \; H_i\right] y_i + \left[\frac{y_i}{y}\right] \bar{x}$$

$$i = 1...n \tag{22}$$

Since

$$f_i\,(Y) = y_i\left[c_i + \ln\frac{y_i}{\bar{y}}\right]$$

Equation (22) becomes

$$x_{i,gas} = -f_i\,(Y) + \left[\sum_{j=1}^{m}\pi_j\,a_{ij} + \pi_{j+1}\,H_i\right]y_i + \left[\frac{y_i}{\bar{y}}\right]\bar{x} \qquad i = 1\ldots n \qquad (23)$$

Equation (23) gives the calculated values of $x_{i,gas}$ based on the estimated values of $y_{i,gas}$ and the calculated values of the Lagrange multipliers. The computed values of $x_{i,gas}$ will serve as estimates of the values for the next iteration.

The elemental balance, Equation (1), can now be put in terms of guessed values of $y_{i,gas}$ by substituting Equation(23) into it. Then the equation becomes

$$-\sum_{i=1}^{n} a_{ik}\,f_i\,(Y) + \sum_{j=1}^{m}\left[\sum_{i=1}^{n} a_{ik}\,a_{ij}\,y_i\right]\pi_j + \left[\sum_{i=1}^{n} a_{ik}\,H_i\,y_i\right]\pi_{j+1}$$
$$+\left[\sum_{i=1}^{n} a_{ik}\,y_i\right]\frac{\bar{x}}{\bar{y}} + \sum_{i=n+1}^{q} a_{ik}\,X_i = b_k \qquad k = 1\ldots m \qquad (24)$$

to simplify equation (24), it is convenient to define

$$r_{jk} = r_{kj} = \sum_{i=1}^{n}(a_{ik})\,(a_{ij})\,y_i \qquad j,k = 1\ldots m \qquad (25)$$

$$r_{j+1,k} = r_{k,j+1} = \sum_{i=1}^{n} a_{ik}\,H_i\,y_i \qquad k = 1\ldots m \qquad (26)$$

$$\sum_{i=1}^{n} a_{ik}\,y_i = b'_k \qquad k = 1\ldots m \qquad (27)$$

$$\sum_{i=1}^{n} H_i\,y_i = b'_{k+1} \text{ and } u = \bar{y}/\bar{x} \qquad (28)$$

Note that the primes on Equations (27) and (28) denote summation over the gas species only. Substituting Equations (25) through (27) into (24), results in the following expression:

$$\sum_{j=1}^{m} r_{jk}\,\pi_j + r_{j+1,k}\,\pi_{j+1} + b'_k\,u + \sum_{i=n+1}^{q} a_{ik}\,X_i = b_k + \sum_{i=1}^{n} a_{ik}\,f_i\,(Y) \qquad (29)$$

$$k = 1 \ldots m$$

The above represents m equations in the m + 2 + s unknowns. The total number of solid phases at equilibrium is s, and there are m + 1 unknown Lagrange multipliers, π_j's. The additional unknown is u.

It is necessary to obtain s + 2 additional equations to completely define the equilibrium state. An additional equation is obtained by summing over the i's in Equation (23). Thus,

$$\bar{x} = -\sum_{i=1}^{n} f_i\,(Y) + \sum_{j=1}^{m} \left[a_{ij}\,y_i\right]\pi_j + \left[\sum_{i=1}^{n} H_i\,y_i\right]\pi_{j+1} + \left(\frac{\bar{y}}{\bar{\bar{y}}}\right)\bar{x} \qquad (30)$$

Noting that the left hand side of the equation cancels with the last term on the right, and using the definitions given in Equations (27) and (28), Equation (30) simplifies to:

$$\sum_{j=1}^{m+1} b_j\,\pi_j = \sum_{i=1}^{n} f_i\,(Y) \qquad (31)$$

With Equations (29) and (31) these are m + 1 equations in m + 2 + s unknowns. s additional equations are obtained from the condition that at equilibrium the free energy is a minimum, i.e., $\partial G(X)/\partial x_i = 0$. Hence from Equations (17) and (19) we have

$$\sum_{j=1}^{m} a_{ij}\,\pi_j + H_i\,\pi_{j+1} = \left[\frac{\bar{F}_T^{\circ}}{RT}\right]_i \qquad i = n+1 \ldots q \qquad (32)$$

and by defining

$$a_{i,j+1} = \Delta H_i \qquad i=1\ldots q \qquad (33)$$

Equation (32) becomes

$$\sum_{j=1}^{m+1} a_{ij}\,\pi_j = \left[\frac{\bar{F}_T^\circ}{RT}\right]_i \qquad (34)$$

With Equations (29), (31) and (34) we have m + 1 = s equations in m + 2 + s unknown. An additional equation is necessary to completely define the system. This is obtained by substituting Equation (23) into (15) together with the definition of Equation (33), and is

$$-\sum_{i=1}^{n} H_i\, f_i\,(Y) + \sum_{k=1}^{m}\left[\sum_{i=1}^{n} a_{ik}\, a_{i,j+1}\, y_i\right]\pi_j + \sum_{i=1}^{n}\left[a_{i,j+1}\, a_{i,j+1}\, y_i\right]\pi_{j+1}$$

$$+\sum_{i=1}^{n} H_i\, y_i\, u + \sum_{i=n+1}^{q}\Delta H_i\, x_i = b_{j+1} \qquad (35)$$

Equation (35) can be simplified further by the prior definitions of Equations (26), (28) and (33). Thus, Equation (35) becomes:

$$\sum_{k=1}^{m+1} r_{k,j+1}\,\pi_j + b'_{j+1}\,u + \sum_{i=n+1}^{q} a_{i,k+1}\,x_i = b_{j+1} + \sum_{i=1}^{n} a_{i,k+1}\,x_i^{(Y)} \qquad (36)$$

With Equations (29), (31), (34) and (36) we have the m + 2 + s equation to solve for m + 2 + s unknown. These are; m + 1 Lagrange Multiplier, π_j's and s x_i's of the solids or condensed phase. There are m Equations (29), one Equation (31), one Equations (34) and s Equations (36). A summary of the equations in their final form is given below.

$$\sum_{j=1}^{m+1} r_{jk}\,\pi_j + b'_k\,u + \sum_{i=n+1}^{q} a_{ik}\,x_i = b_k + \sum_{i=1}^{n} a_{ik}\,f_i\,(Y) \qquad \begin{array}{l} k=1\ldots m \\ \text{from quation (29)} \end{array}$$

$$\sum_{j=1}^{m+1} r_{j,k}\,\pi_j + b'_k\,u + \sum_{i=n+1}^{q} a_{i,k+1}\,x_i = b_k + \sum_{i=1}^{n} a_{i,k+1}\,x_i(Y) \qquad \begin{array}{l} k=m+1 \\ \text{from quation (36)} \end{array}$$

$$\sum_{j=1}^{m+1} b_j \pi_j + \sum_{i=n}^{n} = \sum_{i=1}^{n} f_i (Y) \qquad \text{from Equation} \quad (31)$$

$$\sum_{j=1}^{m+1} a_{ij} \pi_j = \left[\frac{\overset{-o}{F}}{RT} \right]_i \qquad \begin{array}{l} i=n+1 \ldots q \\ \text{from Equation} \end{array} \quad (34)$$

It should be noted that Equations (29) and (36) have the same form. However, they are shown separately to emphasize the difference between the a_{ik}'s and $a_{i,k+1}$. The a_{ik}'s are the formula numbers, which give the gram atoms of element j in specie i, i.e., for CH_4, a_{ik} for carbon is one and for hydrogen four. But $a_{i,k+1} = H_i$ from the definition of Equation (33).

In Table 1 the above equations are shown in expanded form and Equations (29) and (36) are incorporated into the same general form, which simplifies the computer implementation.

Convergence:

The number of iterations required for convergence in the case of restricted equilibrium was observed to be greater than for the general equilibrium case. It was also observed that restricted equilibrium convergence seemed to be more sensitive to the presence of trace species; these having a delaying effect on convergence.

The convergence procedure used was the same as for the general equilibrium case. A brief discussion follows.

Normally in the iterative procedure, the amount of each specie, x_i, which is calculated at the minimum of the constrained quadratic approximation is used as the next estimate. Following the development of White et.al. (3), TABLE-1

GENERAL EQUATIONS FOR THE SOLUTION OF THE EQUILIBRIUM COMPOSITION OF GAS-CONDENSED MIXTURE BY THE FREE ENERGY MINIMIZATION TECHNIQUE*.

$$r_{11}\ \pi_1 + r_{12}\ \pi_2 + \ldots + r_{1,m+1}\ \pi_{m+1} + b'_1\ u + a_{n+1,1}\ x_{n+1} + \ldots + a_{q,1}\ x_q = b_1 + \sum_{i=1}^{n} a_{i1}\ f_i \quad (Y)$$

$$r_{21}\ \pi_1 + r_{22}\ \pi_2 + \ldots + r_{2,m+1}\ \pi_{m+1} + b'_2\ u + a_{n+1,2}\ x_{n+1} + \ldots + a_{q,2}\ x_q = b_2 + \sum_{i=1}^{n} a_{i2}\ f_i \quad (Y)$$

$$r_{31}\ \pi_1 + r_{32}\ \pi_2 + \ldots + r_{3,m+1}\ \pi_{m+1} + b'_3\ u + a_{n+1,3}\ x_{n+1} + \ldots + a_{q,3}\ x_q = b_3 + \sum_{i=1}^{n} a_{i3}\ f_i \quad (Y)$$

$$r_{41}\ \pi_1 + r_{42}\ \pi_2 + \ldots + r_{4,m+1}\ \pi_{m+1} + b'_4\ u + a_{n+1,4}\ x_{n+1} + \ldots + a_{q,4}\ x_q = b_4 + \sum_{i=1}^{n} a_{i4}\ f_i \quad (Y)$$

$$\vdots$$

$$r_{m+1}\ \pi_1 + r_{m+1,2}\ \pi_2 + \ldots + r_{m+1,m}\ \pi_{m+1}\ b'_{m+1}\ u + a_{n+1,5}\ x_{n+2} + \ldots + a_{q,m}\ x_q = b_5 + \sum_{i=1}^{n} a_{i,m+1}\ f_i \quad (Y)$$

$$b_1\ \pi_1 + b_2\ \pi_2 + \ldots + b_{m+1}\ \pi_{m+1} = \sum_{i=1}^{n} f_i \quad (Y)$$

$$a_{n+1,1}\ \pi_1 + \ldots + a_{n+1,m+1}\ \pi_{m+1} = (\overset{-\circ}{F}/RT)_{n+1}$$

$$a_{n+2,1}\ \pi_1 + \ldots + a_{n+2,m+1}\ \pi_{m+1} = (\overset{-\circ}{F}/RT)_{n+2}$$

$$\vdots$$

$$a_{q,1}\ \pi_2 + a_{q,2}\ \pi_2 + \ldots + a_{q,m+1}\ \pi_{m+1} = (\overset{-\circ}{F}/RT)_q$$

*NOTE THAT EQUATIONS HAVE BEEN WRITTEN FOR MORE THAN A CONDENSED PHASE

$$y_{i,new} = y_{i,old} + \lambda \Delta_i \tag{35}$$

where

$$\Delta_i = x_i - y_{i,old} \tag{36}$$

The free energy function can be expressed in terms of the convergence parameter by substituting $y_{i,new}$ of Equation (35) into Equation (6). The result is,

$$F(\lambda) = \sum_{i=1}^{n} \left[y_i + \lambda\Delta_i \right] \left\{ c_i + \ln \left[(y_i + \lambda\Delta_i) \,/\, (\bar{y} + \lambda\bar{\Delta}) \right] \right\} + \sum_{i=n+1}^{q} \left[y_i + \lambda\Delta_i \right] \left(\bar{F}^{\circ}_T / RT \right)_i \tag{37}$$

where y_i is equivalent to $y_{i,old}$ of Equation (35) and

To determine the direction (increase or decrease) of the free energy function, the derivative of F with respect to λ is examined after every iteration. The derivative is easily computed and is,

$$\frac{dF(\lambda)}{d\lambda} = \sum_{i}^{n} \Delta_i \left[c_i + \ln \left\{ (y_i + \lambda\Delta_i) \,/\, (\bar{y} + \lambda\bar{\Delta}) \right\} \right] + \sum_{i=n+1} \Delta_i \left(\frac{F_T}{RT} \right)_i \tag{38}$$

If the directional derivative, $dF/d\lambda$, is negative, a descent path is followed; that is, the value of the free energy on the following iteration will be less than the previous one. When this procedure is successively followed the minimum is eventually reached. However, when a non-negative value of the directional derivative is obtained, the value of the convergence parameter, λ, is reduced until a negative value of the derivative is obtained.

Computational Procedure:

The iterative procedure is initiated by assuming any positive solution $Y = (y_1, y_2, \ldots y_q)$ which satisfies the material balance equations. The values of f_i's (Y) are then determined by Equations (2) and (5) for the gases and solids respectively, as are the values of r_{jk} by Equations (25) and (26). The system of equations shown in Table 1 are now solved simultaneously. From their solution m + 1 values of the Lagrange multipliers the value of $u(= \bar{x}/\bar{y})$ and s values of $x_{i(solid)}$ are obtained. The values of π_j and u are used in Equation (23) to calculate $x_{i,gas}$. These new values serve as starting estimate for the following iteration.

A brief description of the computer implementation is given in Appendix A.

IV. COMPARISON OF RESULTS AMONG EQUILIBRIUM, RESTRICTED EQUILIBRIUM ANALYSIS AND EXPERIMENTAL RESULTS

The chemical composition of the pyrolysis products resulting from the degradation of a 40 percent nylon, 60 percent phenolic resin ablative composite and computed bu a restricted equilibrium analysis is presented in this section. The computations have been done for two decomposition temperatures because of the uncertainty involved in the properties to calculate the average temperatures. In addition two different energy constraints were used because of uncertainties in the heat of pyrolysis. The assumed average temperatures were 600° and 700°C and the energy constraints were -17,000 and -29,000 calories/gram-mole of polymer which correspond to -228 and -390 BTU/lb of composite. The results are presented in Table-2 and Table-3.

In Table-2 a comparison of restricted equilibrium with the experimental data of Sykes (6,7) is given for two energy constraints (H = -17,000 and -29,000 cal/mole of polymer) at a temperature of 700°C. The results show an order of magnitude agreement with the low molecular weight species identified by Sykes (6,7). These are methane, hydrogen, carbon monoxide, carbon dioxide, water and ammonia. The agreement with the high molecular weight species, phenol, toluene, benzine, etc. was rather poor. The change in the energy constraint, H, from -17,000 to -29,000 cal/mole of polymer

TABLE-2

COMPARISON OF RESTRICTED EQUILIBRIUM ANALYSIS COMPOSITIONS WITH THE EXPERIMENTAL DATA OF SYKES(6,7) FOR A 40% NYLON 60% PHENOLIC RESIN COMPOSITE AT A TEMPERATURE OF 700°C.

Species	Restricted Equilibrium Mass Fraction for H = -29,000 cal/mole of polymer	Restricted Equilibrium Mass Fraction for H = -17,000 cal/mole of polymer	Experimental Mass Reaction
Phenol	10^{-13}	10^{-13}	0.118
Methyl Phenol	-	-	0.064
Dimethyl Phenol	-	-	0.051
Trimethyl Phenol	10^{-13}	10^{-13}	0.041
Benzene	10^{-13}	10^{-13}	0.003
Toluene	10^{-13}	10^{-13}	0.001
Cyclopentanone	-	-	0.029
Methane	0.039	0.036	0.010
Hydrogen	0.060	0.061	0.010
Carbon Monoxide	0.160	0.167	0.021
Carbon Dioxide	0.027	0.024	0.067
Water	0.038	0.036	0.062
NH_3	10^{-4}	10^{-4}	0.002
N_2	.040	.040	-
unidentified	-	-	0.181
Carbon	0.635	0.635	0.340
TOTAL	1.000	1.000	1.000

has different and opposite effects in several of the species. For example, an increase in the value of H had the effect of decreasing the amount of hydrogen, carbon, and carbon monoxide, while increasing the concentrations of carbon dioxide and water. It should be noted that the mass fraction of unidentified plus that of carbon makes up 0.521 of the total mass fraction of the experimental composition, while the restricted equilibrium predicts a mass fraction of 0.634 carbon. It should be further noticed that the mass of nitrogen makes up about four percent of the mixture. No nitrogen was reported in the experimental results (6,7).

In Table-3 a similar comparison is made, but the decomposition zone temperature is taken to be 600°C. Again an order of magnitude agreement is observed among the composition of the lower molecular weight species. Changing H affects the composition in the same fashion as was for the 700°C. case.

In general, restricted equilibrium provided an order of magnitude agreement for the composition of low molecular weight compound. It failed to give any agreement with the higher molecular weight component.

In Table-4 a comparison of restricted equilibrium with the general equilibrium analysis is given. It is shown that the compositions are within an order of magnitude of each other. The only mass fraction that is the same is that of nitrogen, since it is practically an inert, and that of carbon which agrees within one percent.

TABLE-3

COMPARISON OF RESTRICTED EQUILIBRIUM ANALYSIS COMPOSITIONS WITH THE EXPERIMENTAL DATA OF SYKES(6,7) FOR A 40% NYLON, 60% PHENOLIC RESIN COMPOSITE AT A TEMPERATURE OF 700°C.

Species	Restricted Equilibrium Mass Fraction for H = -29,000 cal/mole of polymer	Restricted Equilibrium Mass Fraction for H = -17,000 cal/mole of polymer	Experimental Mass Fraction
Phenol	10^{-13}	10^{-13}	0.118
Methyl Phenol	-	-	0.064
Dimethyl Phenol	-	-	0.051
Trimethyl Phenol	-	-	0.041
Benzene	10^{-17}	10^{-17}	0.003
Toluene	10^{-13}	10^{-13}	0.001
Cycloputanane	-	-	0.029
Methane	0.025	0.024	0.010
Hydrogen	0.065	0.066	0.010
Carbon Monoxide	0.205	0.210	0.021
Carbon Dioxide	0.014	0.012	0.067
Water	0.021	0.019	0.062
NH_3	10^{-4}	10^{-4}	0.002
N_2	0.039	0.038	-
unidentified	-	-	0.181
Carbon	0.631	0.630	0.350

TABLE-4

COMPARISON OF RESTRICTED EQUILIBRIUM ANALYSIS WITH THE GENERAL EQUILIBRIUM ANALYSIS FOR A 40% NYLON, 60% PHENOLIC RESIN COMPOSITE, AT 7000°C AND 1 ATMOSPHERE

Species	Restricted Equilibrium Mass Fraction for H = -29,000 cal/mole of polymer	Equilibrium Composition
Phenol	10^{-13}	10^{-18}
Benzene	10^{-17}	10^{-13}
Toluene	10^{-13}	10^{-13}
Methane	0.025	0.043
Hydrogen	0.065	0.059
Carbon Monoxide	0.205	0.150
Carbon Dioxide	0.014	0.031
Water	0.021	0.043
NH_3	10^{-4}	10^{-4}
N_2	0.039	0.039
C	0.631	0.636

V. ACKNOWLEDGEMENTS

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VII. NOMENCLATURE

Symbol	Description
a_{ij}	Formula numbers giving gram-atoms of jth element in the ith species
b_j	Gram-atoms of jth element in mixtures defined by Equation (1)
b_{j+1}	Defined by Equation (14)
c_i	Function defined by Equation (3)
c_p	Heat capacity
$F(X)$	Free energy function of a mixture as defined by Equation (6)
$(\bar{F}^\circ_T)_i$	Standard molal free energy of species i as a pure substance at temperature T
$(\bar{F}_T)_i$	Molal free energy of species i in a mixture
f_i	Free energy of species i defined by Equations (2) and (5)
$G(X)$	Function defined by Equation (16)
H_i	Enthalpy of species i
$\Delta H_{f,i}$	Standard heat of formation of species i
ΔH_{pyr}	Heat of pyrolysis
$(\bar{H}^\circ_T)_i$	Standard molal enthalpy of species i at temperature T
l	Total number of components in the ablative composite
m	Total number of chemical elements
n	Total number of gaseous species
P	Total pressure of system
P_i	Partial pressure of species i
$Q(X)$	Function defined by Equation (10)
q	Total number of chemical species (gases and solids)
r_{jk}	Defined by Equation (25)
R	Universal gas constant (1.987 cal/gm-mole °K)

Symbol	Description
s	
T	Temperature
T_p	Average temperature of the range over which pyrolysis takes place
T_r	Temperature at which pyrolysis begins
u	
x_i	Moles of species i in the mixture at equilibrium
$\bar{x}$	Total moles of gaseous products at equilibrium defined by Equation (4)
$\bar{y}$	Total moles of gaseous products (assumed value)
y_i	Moles of specie i in the mixture (assumed value)
Greek	
α_i	Activity of species i
Δ_i	Function defined by Equation (7a)
$\bar{\Delta}$	Defined by Equation ( )
δ_{ik}	Kronecker delta ($\delta_{ik} = +1$ for $i = k$ and $\delta_{ik} = 0$ for $i \neq k$)
λ	Parameter of a line through two points
π_j	jth Lagrange multiplier
Subscript	
i	Refers to the species
j	Refers to the elements
T	Refers to absolute temperature
Superscript	
$\circ$	Denotes the standard state (298°K and one atmosphere pressure)
$-$	Denotes per mole

Appendix A

Appendix A contains a copy of the printout of the calculations used in this report. A copy will be furnished by the authors upon request.