A THERMODYNAMIC STUDY OF MULTIPLE REACTION SYSTEMS AT AND NEAR EQUILIBRIUM

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ABSTRACT

The near-equilibrium dynamic behavior of a homogeneous batch chemical reactor in which only one reaction occurs has been studied. The system has been analyzed thermodynamically and kinetically near equilibrium. The equations obtained have been linearized and then solved by means of Laplace transform techniques. The derivation for isobaric case has been presented in detail. The solutions for other cases, which include isothermal, isochoric, and adiabatic, have also been given. One numerical application indicates that the linearized equations can be useful even for protracted time intervals providing the forcing function is sufficiently small.

A general expression for the displacement of extent of reactions and mole fractions for multiple reaction systems near equilibrium has been derived. The displacement of extent of reactions for a two-reaction system which obeys ideal solution laws under isobaric condition has also been given. A numerical example has been worked out. The result agrees with the one obtained by brute force approach.

The condition for a multiple reaction system to obey LeChatelier's theorem is derived. It is shown that for the system to obey the theorem the matrix composed of Onsager phenomenological coefficients must be positive definite.

Expressions for the initial distribution of reactants required to maximize a desired product or to suppress an undesired product of a system of chemical reactions proceeding toward equilibrium have been derived. The system consists of R independent reactions and behaves as an ideal solution. It is assumed that the initial feed contains only the reactants and no inerts are present. Three different cases have been considered. They are isothermal-isobaric, isothermal-isochoric and adiabatic-isobaric. The expressions are implicit and complex so that no direct conclusion can be deduced. However, a numerical example (methane-steam system) shows that the effect of initial feed on the distribution of the final product is significant and deserves attention.

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I. DYNAMIC RESPONSE OF NEAR-EQUILIBRIUM SYSTEMS*

In three previous contributions(7-9), referred to below as I - III, Pings has considered the displacement of the equilibrium chemical yield of a variously constrained system for different types of disturbances. Those results are combined here with first-order linearized kinetics to give the transient response of systems slightly perturbed from an equilibrium state. Although there are many textbook illustrations of dynamic response of chemical reactions utilizing simple relaxation time expressions, there apparently has been no systematic treatment which simultaneously accounts for the kinetics and the thermodynamics. The results obtained below are of admitted limited use because of restriction to conditions near equilibrium. As such, however, they should be useful for verification in the limiting case of generalized numerical and graphical techniques for handling systems farther removed from equilibrium. In addition, the expressions derived here are useful in themselves for certain practical problems where it is known that the system subjected to perturbation does not deviate substantially from equilibrium. An obvious example is the dynamic response of chemical storage vessels in which very slow chemical reactions take place under the influence of diurnal temperature variation.

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A. THERMAL RESPONSE OF A CONSTANT PRESSURE SYSTEM

Thermodynamics

An isobaric closed system will be considered; for example, a homogeneous batch reactor. For purpose of simplification, only one reaction is assumed to occur. By taking the time derivative of equation (I. 33)[#] under isobaric conditions, the following is obtained:

$$\dot{Q} = mC_{P,\xi}\,\dot{T} + \Delta\underset{\sim}{H}\,\dot{\xi} \quad . \tag{1}$$

From equation (I. 11)[##] the following expression may be obtained for the isobaric rate of change of equilibrium extent of reaction with respect to time:

$$\dot{\xi}^{*} = \frac{\Delta\underset{\sim}{H}}{RT^{2}\,\alpha}\;\dot{T} \tag{2}$$

where

$$\alpha = \sum_{k=1}^{n} \nu_k \left(\frac{\partial \ln f_k}{\partial \xi}\right)_{T,P} \quad . \tag{3}$$

[#] $$\frac{\delta q}{ds} = mC_{P,\xi}\frac{dT}{ds} + mh_{T,\xi}\frac{dP}{ds} + \sum_{k=1}^{n} \nu_k M_k \overline{H}_k \frac{d\xi}{ds} \tag{I. 33}$$

[##] $$\frac{d\xi}{ds} = \frac{\left[\sum_{k=1}^{n} \nu_k M_k(\overline{H}/T)\right]\frac{dT}{ds} - \left[\sum_{k=1}^{n} \nu_k M_k \overline{V}_k\right]\frac{dP}{ds}}{RT\sum_{k=1}^{n} \nu_k(\partial \ln f_k/\partial\xi)_{T,P}} \tag{I. 11}$$

The kinetics of the system is now introduced in a simplified form by assuming that the time rate of change of the extent of reaction can be represented by the following equation:

$$\dot{\xi} = k(\xi^* - \xi) \quad . \tag{4}$$

In subsequent treatment it will be assumed that near equilibrium, k, which is an effective relaxation time, may be considered as a constant. This coefficient k involves equilibrium concentrations and various stoichiometric and kinetic coefficients as well as the kinetic rate constant. In Appendix A, two illustrations are given of the reduction of general kinetic expressions to the linearized form of equation (4).

The dynamic response of the system to heat input at constant pressure is determined by the set of simultaneous differential equations given by equations (1), (2), and (4).

Since we restrict ourselves to conditions near equilibrium, quantities such as $C_{p,\xi}$, $(\Delta\underset{\sim}{H}/RT^2)$, and α are treated as constants. An alternative approach would be to develop power series expansions of each such term about its value in the equilibrium state, dropping all but first-order terms. For example, considering for the moment only the variation with temperature of the T^{-2} term on the right-hand side of equation (2),

$$\dot{\xi}^* = \left(\frac{\Delta\underset{\sim}{H}}{RT^2\alpha}\right)^* \left[1 + \frac{T-T^*}{T^*} + \dots\right] \dot{T} \quad . \tag{2'}$$

But we restrict the analysis to cases where $(T-T^*)/T^* \ll 1$ justifying the neglect of higher-order terms. $\Delta\underset{\sim}{H}$ also depends on T and ξ, as does α. However, a general expansion in all of the independent variables of all of the state-dependent coefficients leads to exactly parallel treatment. The range of applicability of the final equations of course depends on the domain of justifiable neglect of the higher-order terms. This is particularly restrictive in the case of coefficient k, which might be reasonably expected to have an exponential behavior in absolute temperature.

Equations (1), (2), and (4) are advantageously solved simultaneously by first taking the Laplace transform of each equation and then solving algebraically for the Laplace transform of the temperature, yielding the following expression:

$$\dot{T}(s) = \frac{T(0)}{s} - \frac{k\Delta\underset{\sim}{H}\left[\xi^{*}(0) - \xi(0)\right]}{mC_{p,\xi}\, s(s+K)} + \frac{1}{mC_{p,\xi}}\,\frac{s+k}{s(s+K)} \times \mathcal{L}\{\dot{Q}\} \qquad (5)$$

where we have defined

$$K = k\left[1 + \frac{(\Delta\underset{\sim}{H})^{2}}{mC_{p,\xi}\, RT^{2}\alpha}\right] . \qquad (6)$$

$\mathcal{L}\{\dot{Q}\}$ represents the Laplace transform of the heat input function.

As examples, four special cases of heat input are considered, namely, a delta function input, constant heat input rate, a sinusoidal heat input function, and a completely arbitrary heat input function.

Delta Function Heat Input

This rate of heat input is taken as

$$\dot{Q} = B\delta(\theta) \tag{7}$$

where $\delta(\theta)$ is the usual delta function and B is a weighting factor. For this type of heat input the Laplace transform of $\dot{Q}$ is simply B, and equation (6) becomes after inversion

$$T = T(0) + \frac{k\Delta \underset{\sim}{H}}{KmC_{p,\xi}} \left[\xi^{*}(0) - \xi(0) \right] \left[e^{-K\theta} - 1 \right] + \frac{B}{mC_{p,\xi}} \left[\left(\frac{K - k}{K} \right) e^{-K\theta} + \frac{k}{K} \right] . \tag{8}$$

Constant Heat Input

In this case the rate of heat input is given by

$$\dot{Q} = W \cdot U(\theta) \tag{9}$$

where $U(\theta)$ is a Heaviside function, and W is a weighting factor. The Laplace transform of Q gives W/s. On substituting and taking the inverse Laplace transform of equation (5), the following expression for the dependence of temperature on time is obtained:

$$T = T(0) + \frac{k\Delta \underset{\sim}{H}}{KmC_{p,\xi}} \left[\xi^{*}(0) - \xi(0) \right] \left[e^{-K\theta} - 1 \right] + \frac{W}{mC_{p,\xi}} \left[\frac{K - k}{K^2} + \frac{k}{K}\theta + \left(\frac{k - K}{K^2} \right) e^{-K\theta} \right] \tag{10}$$

Sinusoidal Heat Input

In this case the heat input is represented by

$$\dot{Q} = A_0 + A_1 \sin(c\theta) \quad . \tag{11}$$

Upon substitution for $\mathcal{L}\{\dot{Q}\}$ and taking the inverse transform, the following is obtained for dependence of temperature on time:

$$\begin{aligned} T = T(0) &+ \frac{k\Delta\underset{\sim}{H}}{KmC_{p,\xi}}\left[\xi^*(0) - \xi(0)\right]\left[e^{-K\theta} - 1\right] \\ &+ \frac{A_0}{mC_{p,\xi}}\left[\frac{K-k}{K^2} + \frac{k}{K}\theta + \frac{k-K}{K^2}\, e^{-K\theta}\right] \\ &+ \frac{A_1 c}{mC_{p,\xi}}\left[\frac{k}{Kc^2} + \frac{K-k}{K(c^2+K^2)}\, e^{-K\theta} \right. \\ &\left. - \frac{Kk+c^2}{c^2(c^2+K^2)}\cos(c\theta) + \frac{K-k}{c(c^2+K^2)}\sin(c\theta)\right] . \end{aligned} \tag{12}$$

or

$$\begin{aligned} T = T(0) &+ \frac{k\Delta\underset{\sim}{H}}{KmC_{p,\xi}}\left[\xi^*(0) - \xi(0)\right]\left[e^{-K\theta} - 1\right] \\ &+ \frac{A_0}{mC_{p,\xi}}\left[\frac{K-k}{K^2} + \frac{k}{K}\theta + \frac{k-K}{K^2}\, e^{-K\theta}\right] \\ &+ \frac{A_1 c}{mC_{p,\xi}}\left[\frac{k}{Kc^2} + \frac{K-k}{K(c^2+K^2)}\, e^{-K\theta} \right. \\ &\left. + \frac{\sqrt{(1+K^2/c^2)(1+k^2/c^2)}}{c^2+K^2}\sin(c\theta - \phi)\right] \quad . \end{aligned} \tag{13}$$

where ϕ is a phase factor.

$$\phi = \tan^{-1}\left[\frac{Kk + c^2}{c(K - k)}\right] \quad . \tag{14}$$

<u>Arbitrary Heat Input</u>

For any arbitrary rate of heat input (including the three previous cases) it is always possible to approximate $\dot{Q}$ as a series of discrete Heaviside functions with proper weighting factors.

$$\dot{Q} = \sum_{k=1}^{n} W_k \, U(\theta - \tau_k) \quad . \tag{15}$$

$U(\theta - \tau_k)$ denotes the Heaviside function, τ_k notes the specific time the k^{th} Heaviside function becomes effective, and W_k the appropriate weighting factor. The inverse Laplace transform of equation (5) becomes:

$$T = T(0) + \frac{k\Delta \underset{\sim}{H}}{KmC_{p,\xi}}\left[\xi^*(0) - \xi(0)\right]\left[e^{-K\theta} - 1\right]$$
$$+ \frac{1}{mC_{p,\xi}}\left[\frac{k - K}{K^2}\left(e^{-K\theta} - 1\right) + \frac{k}{K}\,\theta\right]$$
$$\times \left[\sum_{k=1}^{n} W_k \, U(\theta - \tau_k)\right] \quad . \tag{16}$$

It might be noted that when $n = 1$, and $\tau_k = 0$, equation (16) reduces to equation (10).

B. CHANGE IN PRESSURE DUE TO ISOTHERMAL PERTURBATIONS IN VOLUME

Results similar to those in previous sections may be obtained for other choices of variables. As an example we consider the change in pressure due to imposed perturbations in the volume of a system constrained to constant temperature. From an equation equivalent to (I. 45)[#], the following expression may be obtained for the time rate of change for the total volume of the system due to isothermal change in pressure:

$$\dot{\underline{V}} = \left(\frac{\partial \underline{V}}{\partial P}\right)_{T,\,\xi} \dot{P} + \Delta \underset{\sim}{V}\, \dot{\xi} \quad . \tag{17}$$

Also, from equation (I. 11)[##] the following is obtained for the change in equilibrium yield due to change in pressure:

$$\dot{\xi}^{*} = - \frac{\Delta \underset{\sim}{V}}{RT\alpha} \dot{P} \quad . \tag{18}$$

Equation (4) is also assumed to be applicable in this case. Therefore, the dynamic response of the system is determined by simultaneous solution of equations (4), (17), and (18). Again, coefficients in these three equations may be treated as constants, since we restrict

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[#] $$\left(\frac{\partial \underline{V}}{\partial P}\right)_{T} = \left(\frac{\partial \underline{V}}{\partial P}\right)_{T,\,\xi} + \frac{1}{m} \sum_{k=1}^{n} \nu_k M_k \overline{V}_k \left(\frac{\partial \xi}{\partial P}\right)_{T} \quad . \tag{I. 45}$$

[##] See page 2.

ourselves to conditions only slightly removed from equilibrium. By taking the Laplace transform of the three equations and solving simultaneously for the Laplace transform of the pressure, the following is obtained:

$$\overline{P} = \frac{P(0)}{s} - \left(\frac{\partial V}{\partial P}\right)^{-1}_{T,\xi} \left\{ \frac{k\Delta \underset{\sim}{V}}{s(s+K')}\left[\xi^{*}(0) - \xi(0)\right] + \frac{s+k}{s(s+K')} \mathcal{L}\{\dot{V}\} \right\} \tag{19}$$

where

$$K' = k\left[1 - \frac{(\Delta \underset{\sim}{V})^{2}}{RT\left(\frac{\partial V}{\partial \overline{P}}\right)_{T,\xi} \alpha}\right] \tag{20}$$

We treat only the general case in this instance, by representing the arbitrary volume disturbance in terms of a summation of Heaviside functions:

$$\dot{V} = \sum_{k=1}^{n} W'_{k}\, U(\theta - \tau_{k}) \quad . \tag{21}$$

By substituting equation (21) into equation (19) and taking the inverse Laplace transform, the following is obtained for the dependence of pressure upon time for a prescribed volume disturbance:

$$P = P(0) + \frac{k\Delta \underline{V}}{K'\left(\frac{\partial \underline{V}}{\partial P}\right)_{T,\xi}} \left[\xi^{*}(0) - \xi(0)\right]\left[e^{-K'\partial} - 1\right]$$

$$+ \left(\frac{\partial V}{\partial P}\right)^{-1}_{T,\xi} \left\{ \frac{k - K'}{K'^{2}} \left[e^{-K'\theta} - 1\right] + \frac{k}{K'}\,\theta \right\}$$

$$\times \left\{ \sum_{k=1}^{n} W'_{k}\, U(\theta - \tau_{k}) \right\} . \qquad (22)$$

C. OTHER VARIABLES

Other variables and constraints have been studied. Since the derivations are similar to the ones shown in the previous two sections, the details of the derivatives are not given. However, the results (including the ones shown in previous sections) are summarized in Table I.

Inspection of these equations will reveal that they explicitly include terms to account for the fact that the system may not be in a state of equilibrium at time zero, namely the difference $\xi^{*}(0) - \xi(0)$. If the system is initially at chemical equilibrium when disturbed, those terms will of course disappear in all of the equations derived above.

D. EXAMPLE

As an illustration of the possible use of the equations, we compare the predictions of equation (10) with the results obtained by stepwise numerical solution of the rigorous kinetic and thermodynamic equations for a specific system. The following reaction was studied:

$$2HI \rightleftarrows H_2 + I_2 \quad .$$

A total weight of 127.92 grams of the equilibrium mixture initially at 850° K was considered. Two examples were worked out, one involving a heat input of two calories per second and another of four calories per second. The results obtained by the numerical solution are compared in Figure 1 with predictions from equation (10). For sufficiently small values of the perturbation function the linearized equations apparently may be used for extensive time intervals after the disturbance. For larger values of the perturbing function, the equations still may be useful for short time intervals following the perturbation, as indicated by the upper curve in Figure 1.

E. SUMMARY

The near-equilibrium dynamic behavior of a homogeneous batch chemical reactor in which only one reaction occurs has been studied. The system has been analyzed thermodynamically and kinetically near equilibrium. The equations obtained have been linearized and then solved by means of Laplace transform techniques. The derivation for isobaric case has been presented in detail. The solutions for other cases, which include ithothermal, isochoric, and adiabatic, have also been given. One numerical application indicates that the linearized equations can be useful even for protracted time intervals providing the forcing function is sufficiently small.

II. DISPLACEMENT OF EQUILIBRIUM EXTENT OF REACTION FOR MULTIPLE REACTION SYSTEMS NEAR EQUILIBRIUM

In this section the displacement of chemical equilibrium with respect to changes in physical states of multiple reaction systems is studied. Pings(7-9) has investigated this problem for one-reaction systems in detail. Similar treatments can be found elsewhere(4, 16). The discussions presented herein are restricted to the effect of temperature and pressure to a closed multiple reaction system. However, the extension to the effect of other variables, such as volume, enthalpy, and entropy, is apparent.

A. DERIVATION

The system can be represented by the following set of equations:

$$\sum_{k=1}^{n} \nu_{ik} J_k = 0 , \qquad i = 1, \ldots, R \quad . \tag{23}$$

At equilibrium, the following conditions must be met simultaneously.

$$\sum_{k=1}^{n} \nu_{ik} M_k \mu_k = 0 , \qquad i = 1, \ldots, R \quad . \tag{24}$$

Dividing each term of equation (24) by the absolute temperature, T, and then differentiating it with respect to a general variable, s, gives

$$\sum_{k=1}^{n} \nu_{ik} M_k \frac{d(\mu_k/T)}{ds} = 0 , \qquad i = 1, \ldots, R \quad . \tag{25}$$

Since the chemical potential, μ, may be expressed as a function of T, P, and ξ_i, equation (25) can be rewritten in the following form.

$$\sum_{k=1}^{n} \nu_{ik} M_k \left(\frac{\partial(\mu_k/T)}{\partial T}\right)_{P,\check{\xi}_i} \frac{dT}{ds} + \sum_{k=1}^{n} \nu_{ik} M_k \cdot \left(\frac{\partial(\mu_k/T)}{\partial P}\right)_{T,\check{\xi}_i} \frac{dP}{ds} + \sum_{j=1}^{R} \sum_{k=1}^{n} \nu_{ik} M_k \left(\frac{\partial(\mu_k/T)}{\partial \check{\xi}_j}\right)_{T,P,\check{\xi}_i} \cdot \frac{d\check{\xi}_j}{ds} = 0 , \quad i = 1,\ldots,R \quad . \tag{26}$$

The partial derivatives of the chemical potential can be expressed in terms of other thermodynamic variables as in the following$^{(7)}$.

$$\sum_{k=1}^{n} \nu_{ik} M_k \left(\frac{\partial(\mu_k/T)}{\partial T}\right)_{P,\check{\xi}_i} = -\frac{\Delta H_i}{T^2} \tag{27}$$

$$\sum_{k=1}^{n} \nu_{ik} M_k \left(\frac{\partial(\mu_k/T)}{\partial P}\right)_{T,\check{\xi}_i} = \frac{\Delta V_i}{T} \tag{28}$$

$$\sum_{k=1}^{n} \nu_{ik} M_k \left(\frac{\partial(\mu_k/T)}{\partial \check{\xi}_j}\right)_{T,P,\check{\xi}_i} = R \cdot \sum_{k=1}^{n} \nu_{ik} \left(\frac{\partial \ln f_k}{\partial \check{\xi}_j}\right)_{T,P,\check{\xi}_i} , \quad i = 1,\ldots,R \tag{29}$$

where

$$\Delta H_i = \sum_{k=1}^{n} \nu_{ik} M_k \bar{H}_k \tag{30}$$

and

$$\Delta V_i = \sum_{k=1}^{n} \nu_{ik} M_k \overline{V}_k \quad . \tag{31}$$

The overhead-bar indicates partial quantities.

Substituting equations (27), (28), and (29) into equation (26) gives

$$\frac{\Delta V_i}{RT} \cdot \frac{dP}{ds} - \frac{\Delta H_i}{RT^2} \cdot \frac{dT}{ds} + \sum_{j=1}^{R} \sum_{k=1}^{n} \nu_{ik} \left(\frac{\partial \, \ell n \, f_k}{\partial \check{\xi}_j} \right)_{T,P,\check{\xi}_\ell} \cdot \frac{d\check{\xi}_j}{ds} = 0 \; ,$$

$$i = 1, \ldots, R \quad . \tag{32}$$

This equation can be written in matrix form as follows

$$CZ = B \tag{33}$$

or

$$Z = C^{-1} B \tag{33a}$$

where C is a matrix of rank R with elements

$$c_{ij} = \sum_{k=1}^{n} \nu_{ik} \left(\frac{\partial \, \ell n \, f_k}{\partial \check{\xi}_j} \right)_{T,P,\check{\xi}_\ell} \quad , \tag{34}$$

Z is a column vector with elements

$$z_j = \frac{d\check{\xi}_j}{ds} \quad , \tag{35}$$

and B is a column vector with elements

$$b_i = \frac{\Delta H_i}{RT^2} \cdot \frac{dT}{ds} - \frac{\Delta V_i}{RT} \cdot \frac{dP}{ds} \quad . \tag{36}$$

Equation (32) is a general expression which relates the changes in temperature and pressure with the changes in equilibrium extent of reactions of a closed, multiple reaction system.

Two useful special cases can be derived instantly from equation (32).

$$\sum_{j=1}^{R} \sum_{k=1}^{n} \nu_{ik} \left(\frac{\partial \ln f_k}{\partial \check{\xi}_j} \right)_{T,P,\check{\xi}_\ell} \left(\frac{\partial \check{\xi}_j}{\partial T} \right)_{P,\check{\xi}_\ell} - \frac{\Delta H_i}{RT^2} = 0 \ ,$$

$$i = 1, \ldots, R \tag{37}$$

$$\sum_{j=1}^{R} \sum_{k=1}^{n} \nu_{ik} \left(\frac{\partial \ln f_k}{\partial \check{\xi}_j} \right)_{T,P,\check{\xi}_\ell} \left(\frac{\partial \check{\xi}_j}{\partial P} \right)_{T,\check{\xi}_\ell} + \frac{\Delta V_i}{RT} = 0 \ ,$$

$$i = 1, \ldots, R \quad . \tag{38}$$

Equation (37) predicts the isobaric change of equilibrium extent of reactions with respect to temperature and equation (38) gives the isothermal change of equilibrium extent of reaction due to the change in pressure. Although the use of extent of reaction as one of the state variables in the study of problems involving chemical reactions has been widely accepted in academic circles, changes in mole fractions are, in most cases, of primary concern to practicing engineers. Therefore, it is also convenient to have expressions relating mole fractions with extent of reactions.

Let us assume that initially the system is composed of m_j^o moles of jth component and

$$m^o = \sum_{j=1}^{n} m_j^o \quad . \tag{39}$$

After the chemical reactions have taken place and the equilibrium state is reached, the number of moles of jth component becomes

$$m_j = m_j^o + \sum_{i=1}^{R} \nu_{ij} \xi_i \quad . \tag{40}$$

Consequently the total number of moles in the system changes to

$$m = m^o + \sum_{i=1}^{R} \sum_{j=1}^{n} \nu_{ij} \xi_i \tag{41}$$

and the mole fraction of j^{th} component can be expressed as

$$y_j = \frac{m_j}{m} = \frac{m_j^o + \sum_{i=1}^{R} \nu_{ij} \xi_i}{m^o + \sum_{i=1}^{R} \sum_{j=1}^{n} \nu_{ij} \xi_i} \tag{42}$$

or

$$y_j = \frac{y_j^o + \sum_{i=1}^{R} \nu_{ij} \check{\xi}_i}{1 + \sum_{i=1}^{R} \sum_{j=1}^{n} \nu_{ij} \check{\xi}_i} \tag{42a}$$

where

$$\check{\xi}_i = \xi_i / m^o \quad . \tag{43}$$

Differentiating equation (42a) with respect to a general variable, s, and then rearranging, one gets

$$\frac{dy_j}{ds} = \frac{1}{Q'^2} \sum_{i=1}^{R} \left[\nu_{ij} - y_j^o \nu_i^{(n)} \right] \frac{d\check{\xi}_i}{ds} , \quad j = 1, \ldots, n \quad . \tag{44}$$

For convenience, this can be written into the following form.

$$Y = \frac{1}{Q'^2} V^T Z \tag{45}$$

where elements

$$Y = \begin{pmatrix} dy_1/ds \\ dy_2/ds \\ \vdots \\ dy_n/ds \end{pmatrix} \tag{46}$$

$$Q' = 1 + \sum_{i=1}^{R} \sum_{j=1}^{n} \nu_{ij} \check{\xi}_i \tag{47}$$

and V is a R×n matrix with elements

$$V_{ij} = \nu_{ij} - y_j^o \nu_i^{(n)} \quad . \tag{48}$$

Equation (44) relates changes in extent of reactions with changes in mole fractions for a closed, multiple reaction system.

Combining equation (33a) and (45) yields

$$Y = \frac{1}{Q'^2} V^T C^{-1} B \quad . \tag{49}$$

This is the expression which explicitly relates the changes in equilibrium mole fractions with changes in temperature and pressure. Equations (33) and (49) are useful in thermodynamic studies involving chemical changes along the equilibrium path. These expressions are explicit and the only difficulty involved in the application is the evaluation of thermodynamic quantities, ΔH_i, ΔV_i, and $(\partial \ell n\, f_k / \partial \check{\xi}_j)_{T, P, \check{\xi}_\ell}$. These quantities are state variables and, hence, depend only on the thermodynamic state of the system. However, the degree of complexity in the evaluation of these quantities depends greatly upon the nature of the system. A thorough discussion on the evaluation of these quantities has been given by Pings(7).

In order to demonstrate how equation (33) can be transformed into a usable form, let us consider here a simple case. Suppose we wish to find out the temperature derivative of equilibrium extent of reaction of a two-reaction system under isobaric conditions. Let us further assume that the system can be treated as an ideal solution. As a consequence, the following relationships exist:

$$\left.\begin{aligned} f_j &= y_j f_j^{\circledast} \\ \overline{V}_j &= V_j \\ \overline{H}_j &= H_j \end{aligned}\right\} \tag{50}$$

It follows that*

$$\left(\frac{\partial \ln f_k}{\partial \check{\xi}_j}\right)_{T,P,\check{\xi}_\ell} = \frac{1}{Q'}\left[\frac{\nu_{jk}}{y_k} - \sum_{s=1}^{n} \nu_{js}\right] \quad . \tag{51}$$

Substituting equation (51) into equation (37) gives

$$\begin{aligned} \frac{1}{Q'}\Bigg\{\sum_{k=1}^{n} \nu_{1k}\left[\frac{\nu_{1k}}{y_k} - \sum_{s=1}^{n} \nu_{1s}\right]\left(\frac{\partial \check{\xi}_1}{\partial T}\right)_{P,\check{\xi}_2} & \\ + \sum_{k=1}^{n} \nu_{1k}\left[\frac{\nu_{2k}}{y_k} - \sum_{s=1}^{n} \nu_{2s}\right]\left(\frac{\partial \check{\xi}_2}{\partial T}\right)_{P,\check{\xi}_1}\Bigg\} &= \frac{\Delta H_1}{RT^2} \end{aligned} \tag{52}$$

$$\begin{aligned} \frac{1}{Q'}\Bigg\{\sum_{k=1}^{n} \nu_{2k}\left[\frac{\nu_{1k}}{y_k} - \sum_{s=1}^{n} \nu_{1s}\right]\left(\frac{\partial \check{\xi}_1}{\partial T}\right)_{P,\check{\xi}_2} & \\ + \sum_{k=1}^{n} \nu_{2k}\left[\frac{\nu_{2k}}{y_k} - \sum_{s=1}^{n} \nu_{2s}\right]\left(\frac{\partial \check{\xi}_2}{\partial T}\right)_{P,\check{\xi}_1}\Bigg\} &= \frac{\Delta H_2}{RT^2} \quad . \end{aligned} \tag{53}$$

Solving equations (52) and (53) simultaneously one obtains

$$\left(\frac{\partial \check{\xi}_1}{\partial T}\right)_{P,\check{\xi}_2} = \frac{Q'}{RT^2}\left\{\frac{\Delta H_1 \alpha_{22} - \Delta H_2 \alpha_{12}}{\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21}}\right\} \tag{54}$$

$$\left(\frac{\partial \check{\xi}_2}{\partial T}\right)_{P,\check{\xi}_1} = \frac{Q'}{RT^2}\left\{\frac{\Delta H_2 \alpha_{11} - \Delta H_1 \alpha_{21}}{\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21}}\right\} \tag{55}$$

---

*The derivation of this equation is given in Appendix B.

where

$$
\begin{aligned}
\alpha_{11} &= \sum_{k=1}^{n} \nu_{1k} \left[\frac{\nu_{1k}}{y_k} - \sum_{s=1}^{n} \nu_{1s} \right] \\
\alpha_{12} &= \sum_{k=1}^{n} \nu_{1k} \left[\frac{\nu_{2k}}{y_k} - \sum_{s=1}^{n} \nu_{2s} \right] \\
\alpha_{21} &= \sum_{k=1}^{n} \nu_{2k} \left[\frac{\nu_{1k}}{y_k} - \sum_{s=1}^{n} \nu_{1s} \right] \\
\alpha_{22} &= \sum_{k=1}^{n} \nu_{2k} \left[\frac{\nu_{2k}}{y_k} - \sum_{s=1}^{n} \nu_{2s} \right] .
\end{aligned}
\tag{56}
$$

B. EXAMPLE

A numerical example is worked out to show the computational scheme and to verify the correctness of the displacement equation. The application to practical problems has been pointed out by Pings(7). The steam-hydrocarbon process is considered. The system consists of two independent reactions:

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \tag{R-2}$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{R-3}$$

It is assumed that initially the system is at equilibrium. The temperature of the system is then perturbed under isobaric conditions. The temperature derivative of the equilibrium extent of reaction at constant pressure can be obtained from two different approaches. The first one is by the use of equation (37). The second one is to evaluate the equilibrium extent of reaction at the vicinity of the initial temperature and then graphically evaluate the numerical value of the temperature derivative of equilibrium extent of reaction at constant pressure. Both approaches are being used in this example. To perform either of the computations, it is essential to first compute the equilibrium extent of reaction. In order to do this, let us assume, for simplicity, that the system can be treated as an ideal solution. Equation (24) can then be transformed* into

$$\left.\begin{aligned} &\sum_{i=1}^{n} \nu_i \ln \left[\frac{y_i^o + \nu_i \check{\xi}_1 + \eta_i \check{\xi}_2}{1 + \check{\xi}_1 \sum\limits_{i=1}^{n} \nu_i + \check{\xi}_2 \sum\limits_{i=1}^{n} \eta_i} \right] + g_1' = 0 \\ &\sum_{i=1}^{n} \eta_i \ln \left[\frac{y_i^o + \nu_i \check{\xi}_1 + \eta_i \check{\xi}_2}{1 + \check{\xi}_1 \sum\limits_{i=1}^{n} \nu_i + \check{\xi}_2 \sum\limits_{i=1}^{n} \eta_i} \right] + g_2' = 0 \end{aligned}\right\} \tag{57}$$

where

$$g_1' = \sum_{i=1}^{n} \nu_i \left(\frac{F_i^o}{RT} + \ln f_i^o \right) \tag{58}$$

$$g_2' = \sum_{i=1}^{n} \eta_i \left(\frac{F_i^o}{RT} + \ln f_i^o \right) \tag{59}$$

and ν_i and η_i are stoichiometric coefficients for reactions 1 and 2

---

[*] See page 34.

respectively, taken as positive for products, negative for reactants, and zero for components not having a part in the reaction. Equation (57) is then solved simultaneously for $\check{\xi}_1$ and $\check{\xi}_2$. Since the explicit solutions are not possible to obtain, the iterative method of computation is employed.

The Newton-Raphson method is used to obtain the solution. The description of the method can be found elsewhere(6). Computer programs for the IBM 7094 digital computer have been prepared for the computational schemes mentioned before. Appendix C shows the outline of these procedures.

The initial state of $T = 1000^\circ$ K and $P = 1$ atm. is taken. Thermodynamic data used are listed in Table II. Table III gives the temperature derivative of equilibrium extent of reaction at constant pressure of both reactions for different initial mole fraction distributions. Table IV and V give equilibrium extent of reaction for different temperature levels at $P = 1$ atm. for reactions 2 and 3, respectively. These results are plotted as $\check{\xi}_i$ versus T in Figures 2 and 3. The derivatives are then taken graphically and tabulated in Table VI. The agreement between the numerical values given in Table III and Table VI is excellent.

C. SUMMARY

A general expression for the displacement of extent of reactions and mole fractions for multiple reaction systems near equilibrium has been derived. The displacement of extent of reactions for a two-reaction system which obeys ideal solution laws under isobaric condition has also been given. A numerical example has been worked out. The result agrees with the one obtained by brute force approach.

III. STABILITY OF MULTIPLE REACTION SYSTEMS NEAR EQUILIBRIUM

In this section a particular case of thermodynamic theorems of moderation is discussed. It serves partially as an extension of previous section, and at the same time, provides a criterion in the application of LeChatelier's theorem for multiple reaction systems.

Prigogine and Defay (16) have stated that

> Theorems governing the behavior of perturbed systems are known as theorems of restraint or theorems of moderation.
>
> The best known thermodynamic theorem of moderation is that of LeChatelier-Braun, which in the form stated by LeChatelier is:
>
> Any system in chemical equilibrium undergoes, as a result of a variation in one of the factors governing the equilibrium, a compensating change in a direction such that, had this change occurred alone it would have produced a variation of the factor considered in the opposite direction.

Denbigh(4) and Prigogine and Defay(16) have shown the applicability of this theorem to the perturbation of the temperature of single reaction systems. However, multiple reaction case has not been included in the disucssion. In this section we shall extend the discussion to include multiple reaction systems.

A. DERIVATION

Let us assume that the system is a closed, isobaric, and mechanically reversible system and initially at equilibrium state I. The state variables are P, T^I, $\check{\xi}_i^{\,I}$, $i = 1, \ldots, R$. The system is then perturbed by adding (or subtracting) a small amount of heat from its surroundings to a neighboring state II which is not an equilibrium state. The state variables are P, T^{II}, $\check{\xi}_i^{II}$, i = 1, . . . , R and at $\theta = \theta_o$

$$T^{II} = T^{I} + \delta T$$

$$\check{\xi}_i^{II} = \check{\xi}_i^{I} , \qquad i = 1, \ldots, R \quad .$$

Since state II is not an equilibrium state, T^{II} and $\check{\xi}_i^{II}$ will undergo change. The rate of change in temperature is

$$\frac{dT}{d\theta} = \frac{-1}{m\overline{C}_P} \sum_{i=1}^{R} \left(\frac{d\xi_i}{d\theta}\right) \Delta H_i \tag{60}$$

where

m = total weight of the system

$\overline{C}_P$ = average specific heat of the system

ΔH_i = heat of reaction for i^{th} reaction.

The rate of reaction for each reaction, $\dot{\xi}_i$, at the vicinity of equilibrium state, can be assumed to have the form

$$\dot{\xi}_i = \frac{d\xi_i}{d\theta} = \sum_{j=1}^{R} \ell_{ij} A_j \tag{61}$$

where ℓ_{ij} are Onsager phenomenological coefficients. Expanding A_j near equilibrium and neglecting higher order terms, since A_j at equilibrium equal to zero, one has

$$A_j \Big|_{\theta=\theta_o}^{II} = \sum_{s=1}^{R} \left(\frac{\partial A_j}{\partial \check{\xi}_s}\right) \Bigg|_{\theta=\theta_o}^{II} \left(\check{\xi}_s^{II} - \check{\xi}_s^{II^*}\right) \tag{62}$$

where the superscript, *, denotes equilibrium state. By letting $\Delta\xi_s = \check{\xi}_s - \check{\xi}_s^*$ equation (62) can be transformed into

$$A_j\Big|_{\theta=\theta_o}^{II} = \sum_{s=1}^{R}\left(\frac{\partial A_j}{\partial \check{\xi}_s}\right)\Big|_{\theta=\theta_o}^{II} \Delta\xi_s^{II} \quad . \tag{63}$$

Substituting equation (63) into equation (61) and then rearranging terms gives

$$\mathring{\xi}_i\Big|_{\theta=\theta_o}^{II} = \sum_{s=1}^{R} W_{is}\,\Delta\check{\xi}_s^{II} \ , \qquad i = 1,\ldots,R \tag{64}$$

where

$$W_{is} = \sum_{j=1}^{R} \ell_{ij}\left(\frac{\partial A_j}{\partial \hat{\xi}_s}\right)\Big|_{\theta=\theta_o}^{II} \quad . \tag{65}$$

Combining equation (64) with equation (60) gives

$$\frac{dT}{d\theta}\Big|_{\theta=\theta_o} = \frac{-1}{m\overline{C}_P}\left[\sum_{i=1}^{R}\sum_{s=1}^{R} W_{is}\,\Delta\check{\xi}_s\,\Delta H_i\right] \quad . \tag{66}$$

Dividing both sides by $\Delta T = T^I - T^{II}$ one obtains

$$\frac{1}{\Delta T}\left(\frac{dT}{d\theta}\right)\Big|_{\theta=\theta_o} = \frac{-1}{m\overline{C}_P}\left[\sum_{i=1}^{R}\sum_{s=1}^{R} W_{is}\left(\frac{\Delta\xi_s}{\Delta T}\right)\Delta H_i\right] \quad . \tag{67}$$

Now, note that

$$\frac{\Delta\xi_s}{\Delta T} \equiv z_s \tag{35}$$

where P is kept constant.

Hence,

$$\frac{1}{\Delta T}\left(\frac{dT}{d\theta}\right)\bigg|_{\theta=\theta_o} = \frac{-T^2}{m\overline{C}_P}\left[B^T\ W\ Z\right] \quad . \tag{68}$$

It can readily be shown that

$$\left(\frac{\partial A_i}{\partial \check{\xi}_j}\right)_{T,P,\check{\xi}_\ell} = -RT\sum_{k=1}^{n} \nu_{ik}\left(\frac{\partial\,\ell n\, f_k}{\partial\check{\xi}_j}\right)_{T,P,\check{\xi}_\ell} \quad . \tag{69}$$

Combining equations (34), (65), and (68) it is obtained

$$\frac{1}{\Delta T}\left(\frac{dT}{d\theta}\right)\bigg|_{\theta=\theta_o} = \frac{RT^3}{m\overline{C}_P}\left[B^T\ L\ C\ Z\right] \tag{70}$$

where L is a square matrix of rank R with elements ℓ_{ij}.

Substituting equation (33) into equation (70) gives

$$\frac{1}{\Delta T}\left(\frac{dT}{d\theta}\right)\bigg|_{\theta=\theta_o} = \frac{RT^3}{m\overline{C}_P}\left[B^T\ L\ B\right] \quad . \tag{71}$$

If the system obeys LeChatelier's theorem then when $\Delta T > 0$, T_{II} will increase when $\theta > \theta_o$. Hence, $dT/d\theta > 0$ and

$$\Delta T \left(\frac{dT}{d\theta}\right) > 0 \quad .$$

When $\Delta T < 0$, T_{II} will decrease when $\theta > \theta_o$. Hence, $dT/d\theta < 0$ and

$$\Delta T \left(\frac{dT}{d\theta}\right) > 0 \quad .$$

We may then conclude that for the system to obey LeChatelier's theorem the following condition must be satisfied.

$$L > 0 \quad . \tag{72}$$

In other words, the matrix L must be positive definite.

For a two-reaction system the condition becomes[5]

$$\left.\begin{array}{l} \ell_{11} > 0 \\ \ell_{22} > 0 \\ \ell_{11}\ell_{22} - \ell_{12}\ell_{21} > 0 \end{array}\right\} \tag{73}$$

B. SUMMARY

The condition for a multiple reaction system to obey LeChatelier's theorem is derived. It is shown that for the system to obey the theorem the matrix composed of Onsager phnomenological coefficients must be positive definite.

IV. OPTIMIZATION OF EQUILIBRIUM YIELD FOR MULTIPLE REACTION SYSTEMS

One of the most important phases of the modern engineering techniques is to provide means so that the natural resources are utilized in the most economical way. In chemical industries this may imply to the selection of a series of operations in a process or a set of conditions for an operation so as to maximize profit or production, or to minimize cost, resources, or time.

The application of mathematical techniques to explore the "optimum" conditions can be traced all the way back to the ages of Newton and Lagrange. The classical techniques include Lagrangian multiplier method and the calculus of variations. Recently, mainly due to the introduction of new mathematical techniques such as the maximum principle(15), the dynamic programming(1), and the linear programming(2), and the ready accessibility of large scale digital computers, the research activities in this field have been very vigorous. Reviews(17-19) on the scope of the activity are available. The content of this work is directed to a class of problems in chemical engineering which has not been attracting many attentions but is a rather important one in industrial practice.

De Donder and Van Lerberghe(3) and Prigogine and Defay(4) have shown that the equilibrium yield of a chemical reaction, which observes ideal solution laws, is maximized when the reactants are brought together according to the stoichiometric ratios in molal basis. Pings(10-14) has extended the treatment to many practical cases.

In this section a closed, multiple reaction system conforming to ideal solution laws is studied. Expressions for the initial distribution of mole fractions of reactants maximizing a performance index which is a linear function of extent of reaction are derived. Three different cases are studied, namely isothermal-isobaric, adiabatic-isobaric, and isothermal-isochoric. The adiabatic-isobaric case will be treated in detail. Since the thermodynamics and the mathematics involved in each case are similar, only the results of other cases are presented.

A. THERMODYNAMICS

Consider an adiabatic-isobaric system with n chemical species and R independent reactions. The chemical reactions taking place in the system can be expressed by

$$\sum_{j=1}^{n} \nu_{ij} J_j = 0 , \qquad i = 1, \ldots, R \tag{74}$$

where J_j is the chemical symbol of j^{th} species and ν_{ij} is the stoichiometric coefficient of j^{th} species in i^{th} reaction, taken as positive for products, negative for reactants, and zero for the species not participating in the reaction. Without loss of generality the species are so numbered that 1 through L denote reactants and L + 1 through n denote products. Let us assume that initially the system is composed of reactants only. Thus we may write

$$\sum_{j=1}^{L} y_j^o = 1 ;$$

$$y_j^o = 0 , \qquad j = L + 1, \ldots, R \quad . \tag{75}$$

It is also required that

$$y_j \geq 0 , \qquad j = 1, \ldots, n \tag{76}$$

When the reactions take place, the system temperature and mole fractions of the species undergo changes until they reach equilibrium. At equilibrium, the following conditions must be met simultaneously.

$$\sum_{j=1}^{n} \nu_{ij} \mu_j = 0 , \qquad i = 1, \ldots, R \tag{77}$$

where μ_j is the chemical potential of j^{th} species. The chemical potential can be related to the fugacity by

$$\mu_j = \mu_j^{\ominus}(T) + RT \,\ell n\, f_j \tag{78}$$

where $\mu_j^{\ominus}(T)$ is a function only of temperature and f_j is the fugacity of j^{th} component. Combining equations (77) and (78) gives

$$\sum_{j=1}^{n} \nu_{ij} \mu_j^{\ominus}(T) + RT \sum_{j=1}^{n} \nu_{ij} \,\ell n\, f_j = 0 , \qquad i = 1, \ldots, R \tag{79}$$

or simply

$$\sum_{j=1}^{n} \nu_{ij} \,\ell n\, f_j + \frac{\Delta F_i^{\ominus}}{RT} = 0 , \qquad i = 1, \ldots, R \tag{80}$$

where

$$\Delta F_i^{\ominus} = \sum_{j=1}^{n} \nu_{ij}\, \mu_j^{\ominus}(T) \quad . \tag{81}$$

Since the system is closed, isobaric, and mechanically reversible, the change in enthalpy throughout the process is zero. The transition from initial state to final state can be treated as two consecutive steps. The initial feed is formally heated (or cooled) to the final temperature, T, by adding (or removing) some heat Q_1. The reactions then take place at isothermal condition until chemical equilibrium is reached. The heat generated (or consumed) during the course of isothermal reaction is Q_2. It is required that

$$Q_1 + Q_2 = 0 \quad .$$

Hence

$$\sum_{j=1}^{L} \int_{T^o}^{T} y_j^o\, C_{P_j}^o\, dT + \sum_{i=1}^{R} \Delta H_i\, \check{\xi}_i = 0 \quad . \tag{82}$$

An objective function of a multiple reaction system can be expressed by

$$I = \sum_{i=1}^{R} b_i\, \check{\xi}_i \tag{83}$$

where b_i is a weighting factor assigned to i^{th} reaction. The value of b_i may be adjusted to accommodate different objectives. For example, if one of the reactions, say k^{th}, in the system is to be maximized, the performance index, I , becomes

$$I = b_k \check{\xi}_k \tag{84}$$

When one wishes to maximize the yield of a particular product, say k^{th}, then

$$I = \sum_{i=1}^{R} \nu_{ik} \check{\xi}_i \quad . \tag{85}$$

B. ADIABATIC-ISOBARIC CASE

The foregoing discussion can be stated in mathematical terms as follows. It is wished to find the distribution of y_i^o which optimize the performance index

$$I = \sum_{i=1}^{R} b_i \check{\xi}_i \tag{83}$$

under the constraints

$$g_i = \sum_{j=1}^{n} \nu_{ij} \ln f_j + \frac{\Delta F_i}{RT} = 0 \ , \qquad i = 1, \ldots, R \tag{80}$$

$$g_{R+1} = \sum_{j=1}^{L} y_j^o - 1 = 0 \tag{75}$$

$$y_i \geq 0 \ , \qquad j = 1, \ldots, R \tag{76}$$

and

$$g_{R+2} = \sum_{j=1}^{L} \int_{T^o}^{T} y_j^o \, C_{P_j}^o \, dT + \sum_{i=1}^{R} \Delta H_i \check{\xi}_i = 0 \quad . \tag{82}$$

Since the fugacity is a state variable, it can be expressed as a function of the state variables T, P, and y_i. This can be done either in tabular form or as an equation. For simplicity, it is assumed that the system behaves as an ideal solution.

$$f_j = y_j f_j^{\circledast} , \qquad j = 1, \ldots , n \tag{86}$$

where $f_j^{\circledast}$ is the fugacity of pure component and y is the mole fraction. By taking the material balance for j^{th} species one obtains

$$y_j = \frac{y_j^o + \sum_{i=1}^{R} \nu_{ij} \check{\xi}_i}{1 + \sum_{i=1}^{R} \sum_{k=1}^{n} \nu_{ik} \check{\xi}_i} \quad . \tag{87}$$

Substituting equations (86) and (87) into equation (80) gives

$$g_i = \sum_{j=1}^{n} \nu_{ij} \ln \left[\frac{y_j^o + \sum_{\ell=1}^{R} \nu_{\ell j} \check{\xi}_\ell}{1 + \sum_{\ell=1}^{R} \sum_{k=1}^{n} \nu_{\ell k} \check{\xi}_\ell} \right]$$

$$+ \sum_{j=1}^{n} \nu_{ij} \ln f_j^{\circledast} + \frac{\Delta F_i}{RT} = 0 \ ,$$

$$i = 1, \ldots , R \quad . \tag{88}$$

Lagrangian multiplier method is used to obtain the expressions for y_i^o which optimize equation (83) under constraint of equations (75), (76), (82), and (88).

Let

$$\mathcal{L} = I + \sum_{i=1}^{R+2} \lambda_i g_i \tag{89}$$

where λ is an undetermined multiplier. At optimum, the partial derivatives of the Lagrangian, $\mathcal{L}$, with respect to state variables are zero.

$$\frac{\partial \mathcal{L}}{\partial \check{\xi}_i} = b_i + \sum_{k=1}^{R} \lambda_k \left(\frac{\partial g_k}{\partial \check{\xi}_i}\right) + \lambda_{R+2}\left(\frac{\partial g_{R+2}}{\partial \check{\xi}_i}\right) = 0 \ ,$$

$$i = 1, \ldots, R \tag{90}$$

$$\frac{\partial \mathcal{L}}{\partial y_j^o} = \sum_{k=1}^{R} \lambda_k \left(\frac{\partial g_k}{\partial y_j^o}\right) + \lambda_{R+1} + \lambda_{R+2}\left(\frac{\partial g_{R+2}}{\partial y_j^o}\right) = 0 \ ,$$

$$j = 1, \ldots, L \tag{91}$$

$$\frac{\partial \mathcal{L}}{\partial T} = \sum_{k=1}^{R} \lambda_k \left(\frac{\partial g_k}{\partial T}\right) + \lambda_{R+2}\left(\frac{\partial g_{R+2}}{\partial T}\right) = 0 \tag{92}$$

The partial derivatives of the constraints with respect to state variables can readily be obtained as following.

$$\left(\frac{\partial g_k}{\partial \check{\xi}_i}\right) = \alpha'_{ki} = \sum_{j=1}^{n} \nu_{kj} \left[\frac{\nu_{ij}}{y_j^o + \sum_{\ell=1}^{R} \nu_{\ell j} \check{\xi}_\ell} - \frac{\sum_{s=1}^{n} \nu_{is}}{1 + \sum_{\ell=1}^{R} \sum_{s=1}^{n} \nu_{\ell s} \check{\xi}_\ell} \right]$$

$$k = 1, \ldots, R \ ; \quad i = 1, \ldots, R \tag{93}$$

$$\left(\frac{\partial g_{R+2}}{\partial \check{\xi}_i}\right) = \Delta H_i \; , \qquad i = 1, \ldots, R \tag{94}$$

$$\left(\frac{\partial g_k}{\partial y_j^o}\right) = \frac{\nu_{kj}}{y_j^o + \sum_{\ell=1}^{R} \nu_{\ell j} \check{\xi}_\ell}$$

$$k = 1, \ldots, R \; ; \qquad j = 1, \ldots, L \tag{95}$$

$$\left(\frac{\partial g_{R+2}}{\partial y_j^o}\right) = \int_{T_o}^{T} C_{P_j} \, dT = \sigma_j$$

$$j = 1, \ldots, L \tag{96}$$

$$\left(\frac{\partial g_k}{\partial T}\right) = -\frac{\Delta H_k}{RT^2} \; , \qquad k = 1, \ldots, R \tag{97}$$

$$\left(\frac{\partial g_{R+2}}{\partial T}\right) = \sum_{j=1}^{L} y_j^o \, C_{P_j}^{\;T} + \sum_{i=1}^{R} \sum_{j=1}^{m} \nu_{ij} \, C_{P_j}^{\;T} \, \check{\xi}_i = \beta' \; . \tag{98}$$

Substituting equations (93) through (98) into equations (90), (91), and (92) gives

$$b_i + \sum_{k=1}^{R} \lambda_k \, \alpha'_{ki} + \lambda_{k+2} \, \Delta H_i = 0 \; , \qquad i = 1, \ldots, R \tag{99}$$

$$\sum_{k=1}^{R} \lambda_k \frac{\nu_{kj}}{y_j^o + \sum_{\ell=1}^{R} \nu_{\ell j} \check{\xi}_\ell} + \lambda_{R+1} + \lambda_{R+2}\, \sigma_j = 0 \; ,$$

$$j = 1, \ldots, L \tag{100}$$

$$- \sum_{k=1}^{R} \lambda_k \frac{\Delta H_k}{RT^2} + \lambda_{R+2}\, \beta' = 0 \quad . \tag{101}$$

Here we have R + L + 1 equations arising from differentiation of the Lagrangian together with R+2 constrained equations. The unknowns are $\check{\xi}_i$, i=1, . . . ,R; y_j, j=1, . . . , L; λ_i, i=1, . . . ,R+2; and T. In other words we have a system of 2R+L+3 equations with 2R+L+3 unknowns.

From equation (101) it is obtained

$$\lambda_{R+2} = \frac{1}{\beta' RT^2} \sum_{k=1}^{R} \lambda_k \, \Delta H_k \quad . \tag{102}$$

Multiplying equation (100) by $y_j^o + \sum_{\ell=1}^{R} \nu_{\ell j} \check{\xi}_\ell$ and then summing up from j=1 to j=L yields

$$\sum_{k=1}^{R} \sum_{j=1}^{L} \lambda_k \nu_{kj} + \lambda_{R+1} \left(1 + \sum_{\ell=1}^{R} \sum_{j=1}^{L} \nu_{\ell j} \check{\xi}_\ell \right)$$

$$+ \lambda_{R+2} \left\{ \sum_{j=1}^{L} \left[\int_{T^o}^{T} y_j^o \, C_{P_j} \, dT \right.\right.$$

$$\left.\left. + \sum_{\ell=1}^{R} \check{\xi}_\ell \int_{T^o}^{T} \nu_{\ell j} \, C_{P_j} \, dT \right] \right\} = 0 \quad . \tag{103}$$

Letting

$$\psi = 1 + \sum_{\ell=1}^{R} \sum_{j=1}^{L} \nu_{\ell j} \check{\xi}_{\ell} \tag{104}$$

$$\phi' = \sum_{j=1}^{L} \left[\int_{T^o}^{T} y_j^o \, C_{P_j} \, dT + \sum_{\ell=1}^{R} \check{\xi}_{\ell} \int_{T^o}^{T} \nu_{\ell j} \, C_{P_j} \, dT \right] \tag{105}$$

and solving equation (103) for λ_{R+1} gives

$$\lambda_{R+1} = -\frac{1}{\psi} \left(\sum_{k=1}^{R} \sum_{j=1}^{L} \lambda_k \nu_{kj} + \lambda_{R+2} \phi' \right) . \tag{106}$$

Rearranging equation (100) one obtains

$$y_j^o = - \frac{\sum_{k=1}^{R} \lambda_k \nu_{kj}}{\lambda_{R+1} + \lambda_{R+2} \sigma_j} - \sum_{\ell=1}^{R} \nu_{\ell j} \check{\xi}_{\ell} . \tag{107}$$

Combining equations (102), (106), and (107) yields

$$y_j^o = \frac{\left[\sum_{k=1}^{R} \lambda_k \nu_{kj} \right] \psi}{\sum_{k=1}^{R} \lambda_k \left[\sum_{\ell=1}^{L} \nu_{k\ell} + \frac{\Delta H_k}{RT^2} \cdot \frac{\phi' - \psi \sigma_j}{\beta} \right]} - \sum_{\ell=1}^{R} \nu_{\ell j} \check{\xi}_{\ell}$$

$$j = 1, \ldots, L \tag{108}$$

Lagrangian multipliers appeared in equation (108) can be obtained by solving equations (99) and (101) simultaneously.

$$\sum_{k=1}^{R} \lambda_k \left(\alpha'_{ki} + \frac{\Delta H_k}{\beta' R T^2} \right) = - b_i , \qquad i = 1, \ldots, R \quad . \tag{109}$$

By letting

$$\Omega_{kj} = \sum_{\ell=1}^{L} \nu_{k\ell} + \frac{\Delta H_k}{RT^2} - \frac{\phi' - \psi \sigma_j}{\beta'} \tag{110}$$

equation (108) can be simplified to

$$y_j^o = \frac{\left[\sum_{k=1}^{R} \lambda_k \nu_{kj} \right] \psi}{\sum_{k=1}^{R} \lambda_k \Omega_{kj}} - \sum_{\ell=1}^{R} \nu_{\ell j} \check{\xi}_\ell , \qquad j = 1, \ldots, L \quad . \tag{111}$$

Equation (111) is the expression for the distribution of initial mole fractions which maximize the equilibrium yield of a multiple reaction system.

Let us consider now the simplest multiple reaction case, namely, a system with two independent reactions. Since R=2, by solving equation (109) one obtains

$$\lambda_1 = \frac{b_2 \gamma_{21} - b_1 \gamma_{22}}{\gamma_{11}\gamma_{22} - \gamma_{12}\gamma_{21}} \tag{112}$$

$$\lambda_2 = \frac{b_1 \gamma_{12} - b_2 \gamma_{11}}{\gamma_{11}\gamma_{22} - \gamma_{12}\gamma_{21}} \tag{113}$$

where

$$\gamma_{ij} = \alpha'_{ij} + \frac{\Delta H_i}{\beta' R T^2} \tag{114}$$

Equation (111) can be rewritten into the following form.

$$y_j^o = \frac{\nu_{1j}\,\psi - \nu_{1j}\,\Omega_{1j}\,\check{\xi}_1 - \nu_{2j}\,\Omega_{1j}\,\check{\xi}_2}{\Omega_{1j} + \frac{\lambda_2}{\lambda_1}\,\Omega_{2j}}$$

$$+ \frac{\nu_{2j}\,\psi - \nu_{2j}\,\Omega_{2j}\,\check{\xi}_2 - \nu_{1j}\,\Omega_{2j}\,\check{\xi}_1}{\frac{\lambda_1}{\lambda_2}\,\Omega_{1j} + \Omega_{2j}} \qquad (115)$$

Substituting equations (112) and (113) into equation (115) gives

$$y_j^o = \frac{\nu_{1j}\,\psi - \nu_{1j}\,\Omega_{1j}\,\check{\xi}_1 - \nu_{2j}\,\Omega_{1j}\,\check{\xi}_2}{\Omega_{1j} + \frac{b_1\gamma_{22} - b_2\gamma_{21}}{b_2\gamma_{11} - b_1\gamma_{12}}\,\Omega_{2j}}$$

$$+ \frac{\nu_{2j}\,\psi - \nu_{2j}\,\Omega_{2j}\,\check{\xi}_2 - \nu_{1j}\,\Omega_{2j}\,\check{\xi}_1}{\Omega_{2j} + \frac{b_2\gamma_{11} - b_1\gamma_{12}}{b_1\gamma_{22} - b_2\gamma_{21}}\,\Omega_{1j}} \;. \qquad (116)$$

C. OTHER CASES

As mentioned previously, expressions of y_j^o for other cases, isothermal-isobaric and isothermal-isochoric, are also obtained. In isothermal-isochoric cases, instead of the adiabatic condition, one has

$$\underline{V} = \text{constant} \quad . \qquad (117)$$

The constraint equation becomes, by assuming perfect gas,

$$g_{R+2} = P - \frac{m^{o} R T}{\underline{V}} \left(1 + \sum_{i=1}^{R} \sum_{j=1}^{n} \nu_{ij} \check{\xi}_{i} \right) \quad . \tag{118}$$

The partial derivatives for the constraints with respect to the state variable, P, are

$$\left(\frac{\partial g_{i}}{\partial P} \right) = \frac{\Delta V_{i}}{RT} \quad , \qquad i = 1, \ldots, R \tag{119}$$

$$\left(\frac{\partial g_{R+2}}{\partial P} \right) = \beta'' = 1 \quad . \tag{120}$$

The expression for y_j^o becomes

$$y_j^{o} = \frac{\left[\sum_{k=1}^{R} \lambda_{k} \nu_{kj} \right] \psi}{\sum_{k=1}^{R} \sum_{j=1}^{L} \lambda_{k} \nu_{kj}} - \sum_{\ell=1}^{R} \nu_{\ell j} \check{\xi}_{\ell} \, , \qquad j = 1, \ldots, L \quad . \tag{121}$$

The Lagrangian multipliers, λ_k, $k=1,\ldots,R$, can be obtained by solving the following set of simultaneous equations.

$$\sum_{k=1}^{R} \lambda_{k} \left(\alpha'_{ki} + \frac{m^{o} \Delta V_{k}}{\underline{V}} \sum_{j=1}^{n} \nu_{ij} \right) + b_{i} = 0 \, ,$$

$$i = 1, \ldots, R \quad . \tag{122}$$

When the system has only two independent reactions equations (121) and (122) can be reduced to

$$y_j^o = \frac{\nu_{1j} + \nu_{1j}\left(\sum_{\ell=1}^{L} \nu_{2\ell}\right)\check{\xi}_2 - \nu_{2j}\left(\sum_{\ell=1}^{L} \nu_{1\ell}\right)\check{\xi}_2}{\sum_{\ell=1}^{L} \nu_{1\ell} + \frac{b_1\gamma'_{22} - b_2\gamma'_{21}}{b_2\gamma'_{11} - b_1\gamma'_{21}} \cdot \left(\sum_{\ell=1}^{L} \nu_{2\ell}\right)}$$

$$+ \frac{\nu_{2j} + \nu_{2j}\left(\sum_{\ell=1}^{L} \nu_{1\ell}\right)\check{\xi}_1 - \nu_{1j}\left(\sum_{\ell=1}^{L} \nu_{2\ell}\right)\check{\xi}_1}{\sum_{\ell=1}^{L} \nu_{2\ell} + \frac{b_2\gamma'_{11} - b_1\gamma'_{12}}{b_1\gamma'_{22} - b_2\gamma'_{21}} \cdot \left(\sum_{\ell=1}^{L} \nu_{1\ell}\right)} ,$$

$$j = 1, \ldots, L \quad . \qquad (123)$$

where

$$\gamma'_{ij} = \alpha'_{ij} + \frac{m\Delta V_k}{\underline{V}} \left(\sum_{j=1}^{n} \nu_{ij}\right) . \qquad (124)$$

For isothermal-isobaric cases the constraint due to the adiabatic condition, equation (82), and the partial derivative of the Lagrangian with respect to temperature, equation (92), do not apply. The final expression of y_j^o has the following form.

$$y_j^o = \frac{\left[\sum_{k=1}^{R} \lambda_k \nu_{kj}\right]\psi}{\sum_{k=1}^{R} \sum_{\ell=1}^{L} \nu_{k\ell}\lambda_k} - \sum_{\ell=1}^{R} \nu_{\ell j}\check{\xi}_\ell ,$$

$$j = 1, \ldots, L \qquad (125)$$

and the Lagrangian multipliers are obtained by solving the following set of simultaneous equations.

$$\sum_{k=1}^{R} \lambda_k \alpha'_{ki} + b_i = 0 \,, \qquad i = 1, \ldots, R \,. \tag{126}$$

It is worth noting that when

$$\Delta H_i = 0 \,, \qquad i = 1, \ldots, R$$

equation (111) reduces to equation (125).

For two-reaction cases equations (125) and (126) can be combined to form

$$y_j^o = \frac{\nu_{1j} + \nu_{1j}\left(\sum_{\ell=1}^{L} \nu_{2\ell}\right)\check{\xi}_2 - \nu_{2j}\left(\sum_{\ell=1}^{L} \nu_{1\ell}\right)\check{\xi}_2}{\sum_{\ell=1}^{L} \nu_{1\ell} + \frac{b_1\alpha'_{22} - b_2\alpha'_{21}}{b_2\alpha'_{11} - b_1\alpha'_{12}}\left(\sum_{\ell=1}^{L} \nu_{2\ell}\right)}$$

$$+ \frac{\nu_{2j} + \nu_{2j}\left(\sum_{\ell=1}^{L} \nu_{1\ell}\right)\check{\xi}_1 - \nu_{1j}\left(\sum_{\ell=1}^{L} \nu_{2\ell}\right)\check{\xi}_1}{\sum_{\ell=1}^{L} \nu_{2\ell} + \frac{b_2\alpha'_{11} - b_1\alpha'_{12}}{b_1\alpha'_{22} - b_2\alpha'_{21}}} \,,$$

$$j = 1, \ldots, L \,. \tag{127}$$

D. COMPUTATION

It is important to point out that the solutions for the distribution of initial mole fractions are implicit. Since some unknown variables are included in the right-hand side of equations (111), (121), and (125), direct evaluation of the numerical values of y_j^o is not possible. However, a simple iterative scheme can be employed, with the aid of a digital computer, to obtain the solution. The iterative procedure involves the following steps. The adiabatic-isobaric case is used as an example.

1. Assume a set of y_j^o, $j=1,\ldots,L$ such that

$$\sum_{j=1}^{L} y_j^o = 1 \quad .$$

2. Assume a temperature T.
3. Compute ΔF_i, $f_j^{\circledast}$ and ΔH_i .
4. Compute extent of reaction $\check{\xi}_i$, $i=1,\ldots,R$ by solving equation (88).
5. Evaluate g_{R+2} by equation (82). If g_{R+2} is not equal to zero, modify T and then go back to step 3.
6. Evaluate λ_k by solving equation (109).
7. Compute y_j^o by equation (111).
8. If the computed y_j^o are not equal to the assumed y_j^o then repeat the whole calculation using the computed y_j^o. Normalize y_j^o if necessary.

E. EXAMPLE

The production of hydrogen by the steam hydrocarbon process is considered. The purpose of this process is to generate hydrogen from light hydrocarbons, such as methane and propane, which can be obtained in abundance from natural gas. The hydrogen is being used for the synthesis of ammonia and hydrogenation. With methane as the raw material the reactions are

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \tag{R-2}$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{R-3}$$

The by-products of the reactions are carbon monoxide and carbon dioxide.

We shall consider two different types of production schedule. The first one is to produce the maximum amount of hydrogen per mole of feed. This will be the optimum policy when the content of impurities in the production stream is not very important. Since carbon monoxide is an active poison for the nickel catalysts employed in many types of hydrogenation operations, the carbon monoxide content of the production stream must be reduced. Hence, in the second type of production schedule only the first reaction will be maximized. The performance index for the first case is

$$I = \check{\xi}_1 + 0.75\,\check{\xi}_2 \tag{128}$$

and that for the second case is

$$I = \check{\xi}_1 \quad . \tag{129}$$

The reactions are assumed to take place at 1000° K and 1 atm. The thermodynamic data required are taken from API Research Project 44. These data are summarized in Table II. The result of computation is given in Table VII. It reveals the following. The maximum hydrogen content in the production stream is 0.68. The molal feed ratio of methane to steam which maximize the hydrogen content is about 1 : 1. By changing the methane to steam ratio from 1 : 1 to 0.29 : 1, the hydrogen content is reduced from 0.68 to 0.53; a reduction of 22%. But the carbon monoxide content is reduced from 0.20 to 0.08; a reduction of 60%.

For the sake of comparison and for general verification of the correctness of the analysis, equation (88) is solved simultaneously for various mole fraction distributions. Objective functions, equations (128) and (129), are plotted in Figure 4 as a function of $y^o_{CH_4}$. The arrows indicate the computed values of $y^o_{CH_4}$ which maximize the objective functions. The agreement is excellent.

F. SUMMARY

Expressions for the initial distribution of reactants required to maximize a desired product or to suppress an undesired product of a system of chemical reactions proceeding toward equilibrium have been derived. The system consists of R independent reactions and behaves as an ideal solution. It is assumed that the initial feed contains only the reactants and no inerts are present. Three different cases have been considered. They are isothermal-isobaric, isothermal-isochoric and adiabatic-isobaric. The expressions are implicit and complex so that no direct conclusion can be deduced. However, a numerical example (methane-steam system) shows that the effect of initial feed on the distribution of the final product is significant and deserves attention.

NOMENCLATURE

A_k	affinity for k^{th} component.
A_0, A_1	constants in the periodic heat input function, equation (11).
a_i	activity of component i.
b_i	i^{th} element in B vector defined by equation (36), Section II.
B	a vector constant coefficient, Section IV.
B	a constant, equation (7).
c_{ij}	an element in C matrix defined by equation (34).
C	a matrix defined on p. 14, Section II.
$C_{p,\xi}$	isobaric molal heat capacity of an unreacting system.
$C_{V,\xi}$	isochoric molal heat capacity of an unreacting system.
c	frequency of periodic heat input.
c_i	concentration of component i.
E	total internal energy.
ΔE	$\sum_{k=1}^{n} \nu_k M_k \tilde{E}_k$.
$\tilde{E}_k$	$(\partial E/m_k)_{T,V,m_i}$.
f	fugacity.
G	defined in footnote to Table I.
g_i	a constraint equation defined in Section IV.
H	specific enthalpy.
$\overline{H}_k$	specific partial enthalpy.
ΔH	$\sum_{k=1}^{n} \nu_k M_k \overline{H}_k$.
I	objective function.

J_k	chemical symbol for k^{th} component.
k	linearized rate constant; see equation (4) and Appendix.
$\overrightarrow{k}_a, \overleftarrow{k}_a$	forward and reverse rate constants based on activities.
$\overrightarrow{k}_c, \overleftarrow{k}_c$	forward and reverse rate constants based on concentrations.
ℓ	Onsager phenomenological coefficient.
M	molecular weight.
m	total number of moles.
n	number of components in a system.
P	pressure.
Q	heat.
Q'	defined by equation (47).
R	universal gas constant.
R	number of independent reactions in a system.
s	Laplace transform variable, Section I.
s	a general variable, Section II.
T	absolute temperature.
$\underline{V}$	total volume.
V	a matrix defined by equation (48), Section II.
$\overline{V}_k$	specific partial volume.
ΔV	$\sum_{k=1}^{n} \nu_k M_k \overline{V}_k$.
W	a constant, equation (9), Section I.
W	defined by equation (65), Section III.
y_i	mole fraction of component.
z	an element in Z vector defined in equation (35).
Z	a vector.

Greek letters:

α	defined by equation (3), Section I.
α_{ij}	defined by equation (56), Section II.
α'_{ij}	defined by equation (93), Section IV.
β	defined in footnote to Table I.
β'	defined in equation (98), Section IV.
δ	the delta function operator.
μ	chemical potential.
Ω	defined by equation (110).
ψ	defined by equation (104).
σ	defined by equation (96).
η_i	kinetic coefficient, Section I.
η_i	stoichiometric coefficient, Section IV.
θ	time.
K, K'	defined by equations (6) and (20).
λ_i	kinetic coefficient, Appendix A.
λ_i	undetermined multiplier, Section IV.
ν_i, ν_{ij}	stoichiometric coefficients.
$\nu_i^{(n)}$	$\sum_{j=1}^{n} \nu_{ij}$.
ξ	extent of reaction.
$\check{\xi}$	ξ / m^o
τ	time.
ϕ	phase lag, equation (14).
ϕ'	defined by equation (105).

Subscripts:

k	refers to component k.
(0)	denotes initial value, i.e., at $\theta = 0$.

Superscripts:

I, II, . . .	points in state space.
o	initial state.
$\ominus$	standard state.
$*$	equilibrium state.
$\circledast$	pure substance.

Operators:

$\dot{F}$	$dF/d\theta$.
R, P, L	indicates summation or multiplication over reactions, products, and reactants, respectively.
Σ	summation.
$\prod$	product.
$\Big\|_{\theta=\theta_o}$	evaluated at $\theta = \theta_o$.
$\mathcal{L}\{\ \}$	Laplace transform operator.

LIST OF REFERENCES

1. Bellman, R., and S. Dreyfus, Applied Dynamic Programming, Princeton University Press, Princeton, New Jersey (1962).

2. Dantzig, G. B., Linear Programming and Extensions, Princeton University Press, Princeton, New Jersey (1963).

3. DeDonder, T., and G. Van Lerberghe, Bull. Sci. Acade. Roy. Belg., Ser. 5, 12, p. 151 (1926).

4. Denbigh, K., The Principles of Chemical Equilibrium, Cambridge at the University Press, London (1963).

5. Frazer, R. A., W. J. Duncan, and A. R. Collar, Elementary Matrices and Some Applications to Dynamic and Differential Equations, Cambridge at the University Press, London (1963).

6. Lapidus, L., Digital Computation for Chemical Engineers, McGraw-Hill, (1962).

7. Pings, C. J., "Thermodynamics of Chemical Equilibrium - I," Chem. Eng. Sci., 16, 181 (1961).

8. Pings, C. J., "Thermodynamics of Chemical Equilibrium - II," Chem. Eng. Sci., 18, 671 (1963).

9. Pings, C. J., "Thermodynamics of Chemical Equilibrium - III," Chem. Eng. Sci. To be published.

10. Pings, C. J., "Optimum Feed Composition in Moderately Dense Gases," I&EC Fundamentals, 2, No. 3, 244-245 (1963).

11. Pings, C. J., "Maximization of Yield in Isothermal Gas Phase Reactions in the Presence of Inerts," I&EC Fundamentals, 2, No. 4, 321-323 (1963).

12. Pings, C. J., "Economic Optimization of Feed Composition," Chem. Eng. Prog., 59, No. 12, 90-92 (1963).

13. Pings, C. J., "Optimization of Initial Composition in Adiabatic Equilibrium Gas-Phase Reactions," A.I.Ch.E. Jour., 10, No. 6, 934-936 (1964).

14. Pings, C. J., "Optimization of Initial Composition, Adiabatic Equilibrium Gas-Phase Reactions in the Presence of Inerts," I&EC Fundamentals, 4, No. 3, 260-264 (1965).

15. Pontryagin, L. S., V. G. Boltyanski, R. V. Gamkrelidze, and E. F. Mischenko, The Mathematical Theory of Optimum Processes, Interscience, New York (1962).

16. Prigogine, E., R. Defay, and D. H. Everett, Chemical Thermodynamics, Longmans, Green and Co., London (1954).

17. Sweeny, R. F., R. S. Davis, and C. D. Hendrix, "Annual Review, Mathematics," I&EC, 57, No. 12, 72-77 (1965).

18. Wilde, D. J., "A Review of Optimization Theory," I&EC, 57, No. 8, 18-31 (1965).

19. Williams, T. J., "Annual Review, Process Control," I&EC, 57, No. 12, 33-43 (1965).

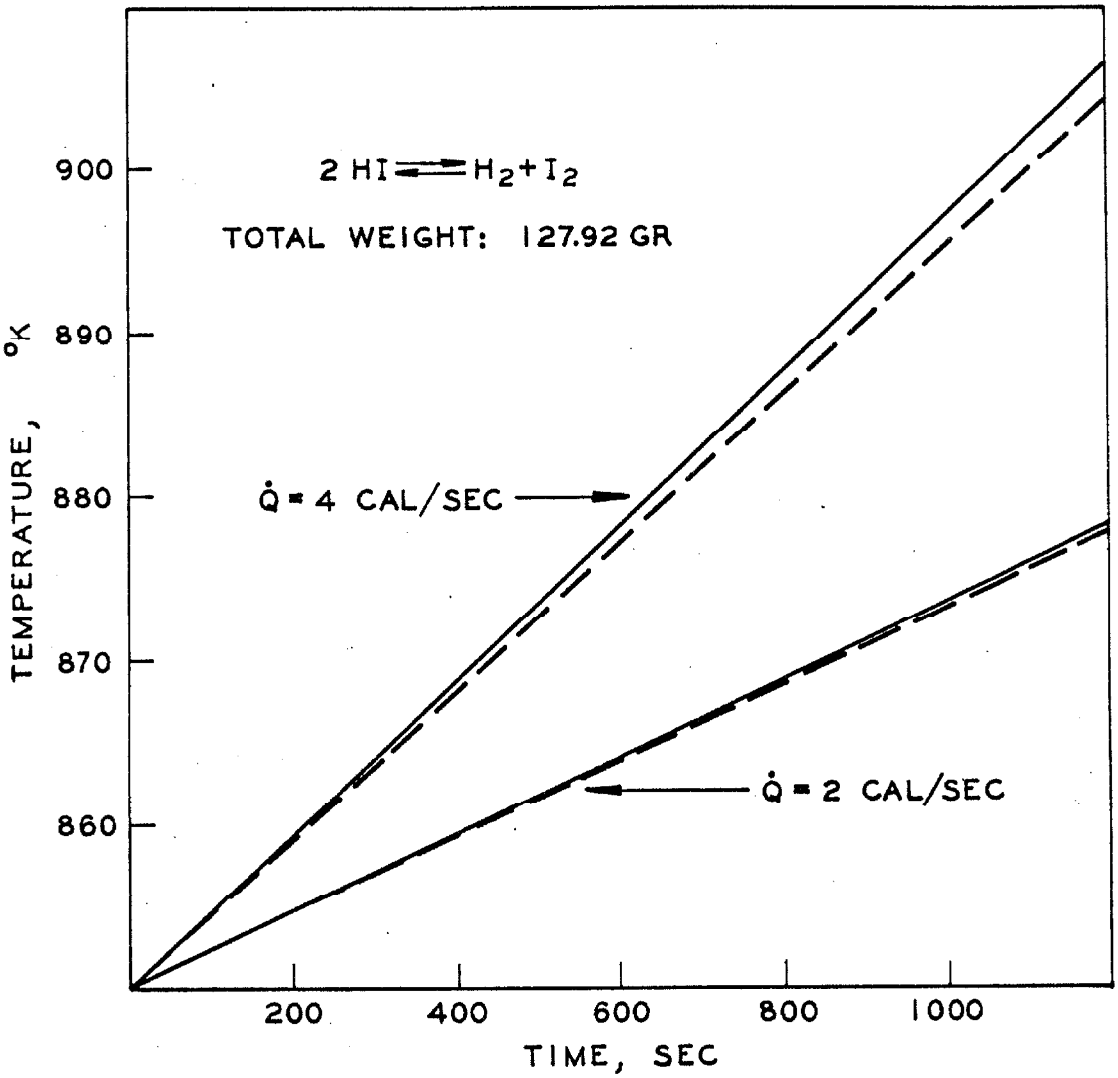


FIG. 1. Comparison of the temperature - time history of mixture HI, H_2, and I_2 initially at equilibrium at 850° K.

- - - - Numerical solution of exact thermodynamic and kinetic equations.

——— Solution of linearized equations as given by equation (10).

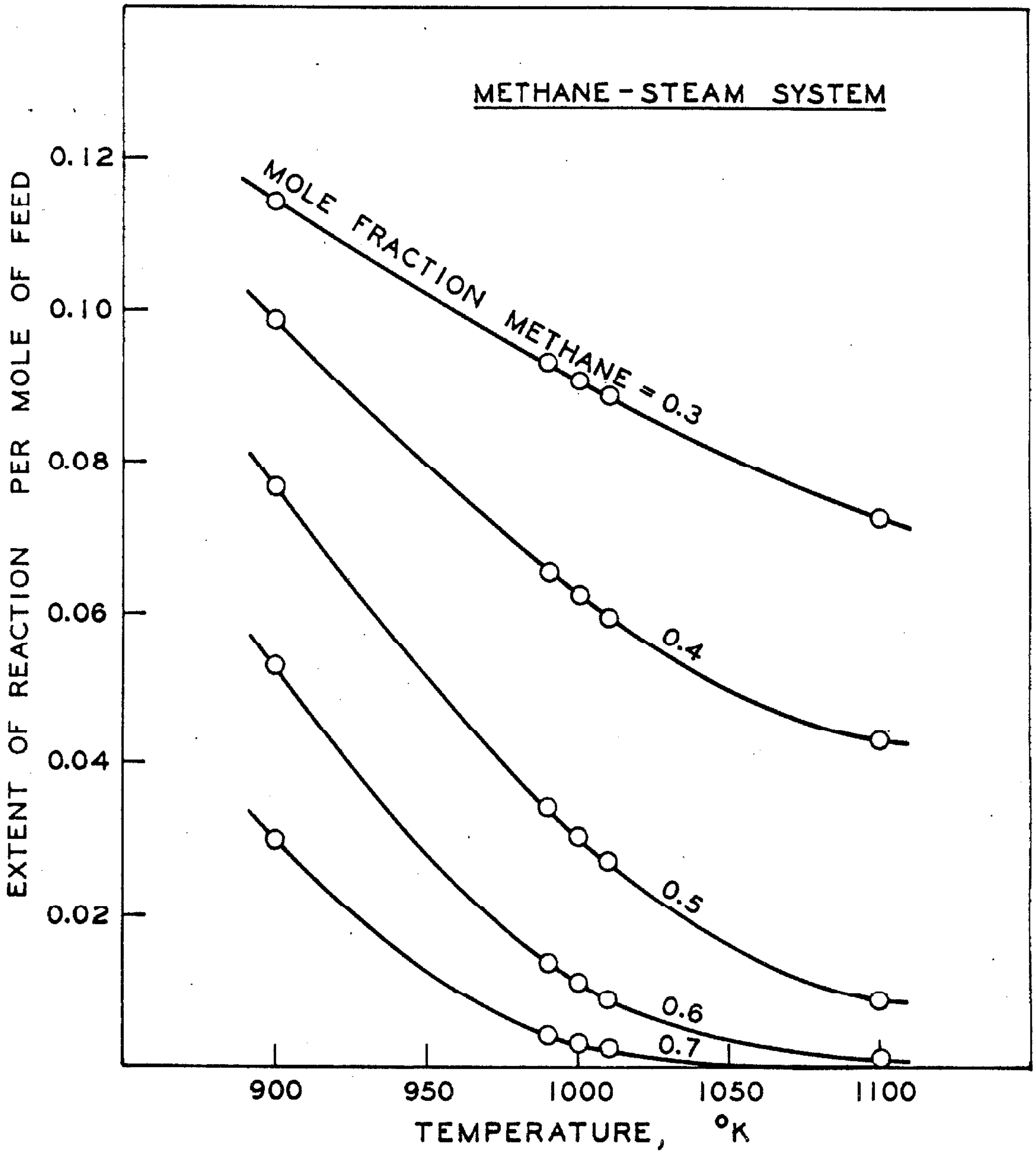


FIG. 2. Equilibrium extent of reaction for the reaction $CH_4 + 2\,H_2O \rightleftharpoons CO_2 + 4\,H_2$ of methane-steam process at 1 atm.

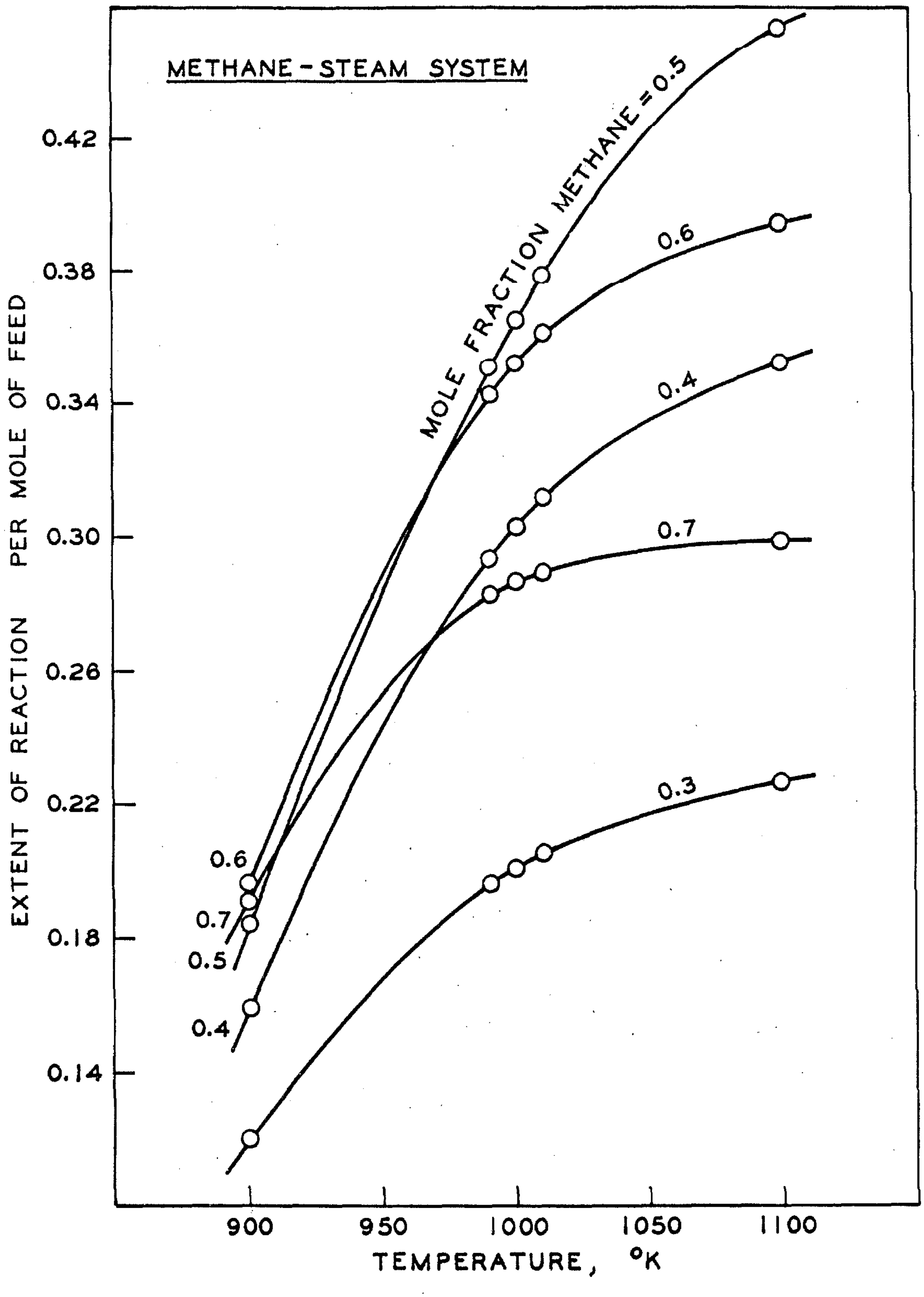


FIG. 3. Equilibrium extent of reaction for the reaction $CH_4 + H_2O \rightleftharpoons CO + 3\ H_2$ of methane-steam process at 1 atm.

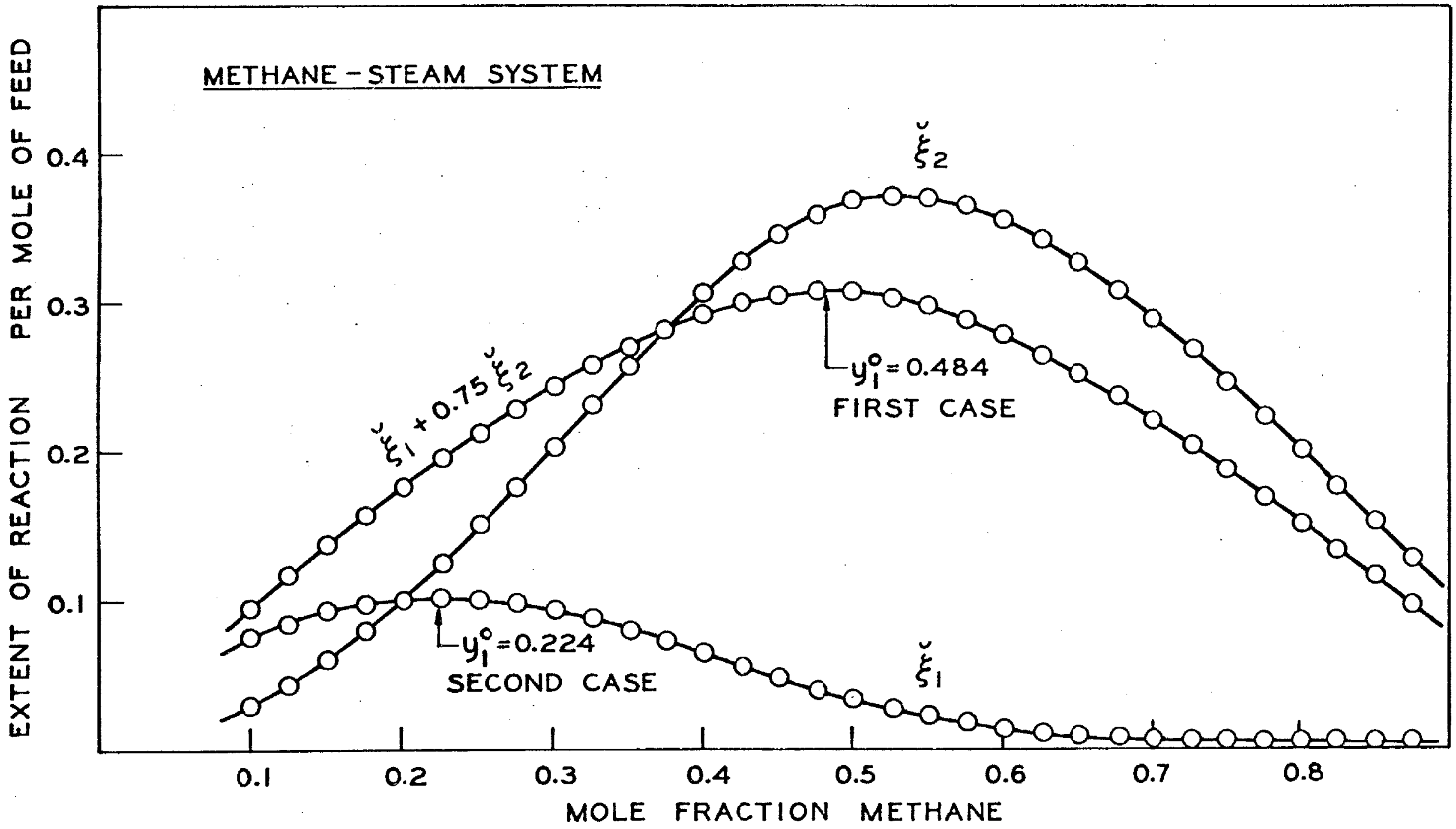


FIG. 4. Plot of equilibrium extent of reaction for methane-steam process versus initial mole fraction of methane.

TABLE I

SUMMARY OF SOLUTIONS TO THE LINEARIZED EQUATIONS

Parameters			Solutions
Con-stant	Input	Per-turbed	
P	$\dot{Q}$	T	$T = T(0) + \frac{k\Delta \underset{\sim}{H}}{KmC_{p,\xi}} \left[\xi^*(0) - \xi(0) \right] \left[e^{-K\theta} - 1 \right]$
			$+ \frac{1}{mC_{p,\xi}} \left[\frac{k - K}{K^2} \left(e^{-K\theta} - 1 \right) + \frac{k}{K} \theta \right] \left[\sum_{i=1}^{n} W_i \, U\left(\theta - \tau_i \right) \right]$
T	$\dot{V}$	P	$P = P(0) + \frac{k\Delta \underline{V}}{K' \left(\frac{\partial \underline{V}}{\partial \underline{\underline{P}}} \right)_{T,\xi}} \left[\xi^*(0) - \xi(0) \right] \left[e^{-K'\theta} - 1 \right]$
			$+ \left(\frac{\partial \underline{V}}{\partial \underline{\underline{P}}} \right)^{-1}_{T,\xi} \left[\frac{k - K'}{K'^2} \left(e^{-K'\theta} - 1 \right) + \frac{k}{K'} \theta \right] \left[\sum_{i=1}^{n} W_i \, U\left(\theta - \tau_i \right) \right]$
V	$\dot{Q}$	T	$T = T(0) + \frac{k\Delta \underset{\sim}{E}}{GmC_{V,\xi}} \left[\xi^*(0) - \xi(0) \right] \left[e^{-G\theta} - 1 \right]$
			$+ \frac{1}{mC_{V,\xi}} \left[\frac{k - G}{G^2} \left(e^{-G\theta} - 1 \right) + \frac{k}{G} \theta \right] \left[\sum_{i=1}^{n} W_i \, U\left(\theta - \tau_i \right) \right]$

TABLE 1--Continued

Parameters			Solutions
Constant	Input	Perturbed	
H	$\dot{P}$	T	$T = T(0) + \frac{k\Delta \underset{\sim}{H}}{KmC_{p,\xi}} \left[\xi^{*}(0) - \xi(0)\right] \left[e^{-K\theta} - 1\right]$ $+ \frac{\underline{V} - T\left(\frac{\partial V}{\partial T}\right)_{P,\xi}}{mC_{p,\xi}} \left[\frac{k' - K}{K^2}\left(e^{-K\theta} - 1\right) + \frac{k'}{K}\theta\right] \left[\sum_{i=1}^{n} W_i\, U\left(\theta - \tau_i\right)\right]$

$$G = k\left[1 + \frac{(\Delta \underset{\sim}{E})^2}{mC_{V,\xi} R T^2 \beta}\right]$$

$$\beta = \sum_{i=1}^{n} \nu_i \left(\frac{\partial\, \ell n\, f_i}{\partial \xi}\right)_{T,V}$$

$$k' = k\left[1 - \frac{(\Delta \underset{\sim}{H})\,(\Delta \underset{\sim}{V})}{\left[\underline{V} - T\left(\frac{\partial V}{\partial T}\right)_{P,\xi}\right] R T \alpha}\right]$$

TABLE II

THERMODYNAMIC DATA FOR STEAM-METHANE PROCESS AT T = 900, 990, 1000, 1010, and 1100°K.

Component	Free Energy of Formation[#]					Heat of Formation[#]
	900	990	1000	1010	1100	1000
CH_4	2.01	4.359	4.61	4.87	7.22	-21.43
H_2O	-47.347	-46.162	-46.030	-45.897	-44.700	-59.214
CO_2	-94.578	-94.607	-94.610	-94.613	-94.637	-94.318
CO	-45.816	-47.729	-47.942	-48.153	-50.053	-26.768
H_2	0	0	0	0	0	0

[#] Kcal/mol.

TABLE III

TEMPERATURE DERIVATIVE OF EQUILIBRIUM EXTENT OF REACTION AT 1 ATM. FOR STEAM-METHANE PROCESS USING EQUATION (37)

$y^o_{CH_4}$	$\left(\frac{\partial \xi_1}{\partial T}\right)_{P,\xi_2}$ #	$\left(\frac{\partial \xi_2}{\partial T}\right)_{P,\xi_1}$ #
0.3	-0.2213×10^{-3}	0.4286×10^{-3}
0.4	-0.2897×10^{-3}	0.9454×10^{-3}
0.5	-0.3579×10^{-3}	0.1386×10^{-2}
0.6	-0.2375×10^{-3}	0.9316×10^{-3}
0.7	-0.8705×10^{-4}	0.3397×10^{-3}

#mol/mol/°K.

TABLE IV

EQUILIBRIUM EXTENT OF REACTION FOR THE REACTION (R-2), ξ_1, OF STEAM-METHANE PROCESS AT 1 ATM.

Initial Mole Fraction for Methane	Temperature in °K.				
	900	990	1000	1010	1100
0.3	0.11413	0.09322	0.09099	0.08884	0.07266
0.4	0.09844	0.06517	0.06220	0.05945	0.04356
0.5	0.07674	0.03422	0.03056	0.02714	0.00876
0.6	0.05295	0.01362	0.01111	0.00892	0.00101
0.7	0.02984	0.00414	0.00317	0.00240	0.00021

TABLE V

EQUILIBRIUM EXTENT OF REACTION FOR THE REACTION (R-3), $\check{\xi}_2$, OF STEAM-METHANE PROCESS AT 1 ATM.

Initial Mole Fraction for Methane	Temperature in °K.				
	900	990	1000	1010	1100
0.3	0.11999	0.19599	0.20049	0.20449	0.22656
0.4	0.15878	0.29356	0.30339	0.31228	0.35240
0.5	0.18439	0.35095	0.36501	0.37839	0.45404
0.6	0.19628	0.34283	0.35260	0.36128	0.39478
0.7	0.19134	0.28293	0.28666	0.28969	0.29891

TABLE VI

TEMPERATURE DERIVATIVE OF EQUILIBRIUM EXTENT OF REACTION AT 1 ATM. FOR STEAM-METHANE PROCESS BY GRAPHICAL METHOD

$y^o_{CH_4}$	$\left(\frac{\partial \check{\xi}_1}{\partial T}\right)_{P,\check{\xi}_2}^{\#}$	$\left(\frac{\partial \check{\xi}_2}{\partial T}\right)_{P,\check{\xi}_1}^{\#}$
0.3	-2.19×10^{-4}	4.25×10^{-4}
0.4	-2.86×10^{-4}	9.36×10^{-4}
0.5	-3.54×10^{-4}	1.372×10^{-3}
0.6	-2.35×10^{-4}	9.225×10^{-4}
0.7	-0.87×10^{-4}	3.38×10^{-4}

#mol/mol/°K.

TABLE VII

COMPUTATIONAL RESULTS FOR THE OPTIMIZATION OF STEAM-METHANE PROCESS UNDER ISOTHERMAL-ISOBARIC CONDITION (T = 1000°K, P = 1 ATM.)

Case	Mole Fraction Feeds		Mole Fraction Products					Extent of Reaction	
	CH_4	H_2O	CH_4	H_2O	CO_2	CO	H_2		
1	0.4838	0.5162	0.0497	0.0482	0.196	0.2010	0.6815	0.03509	0.3598
2	0.2239	0.7761	0.0015	0.3149	0.0692	0.0844	0.5300	0.09988	0.12182

APPENDIX A

LINEARIZATION OF KINETIC EXPRESSIONS

Example I

If the reaction is elementary,

$$\frac{d\xi}{d\theta} = \vec{k}_a \prod_{\text{reactants}} \left[a_i\right]^{-\nu_i} - \overleftarrow{k}_a \prod_{\text{products}} \left[a_i\right]^{\nu_i} \tag{A. 1}$$

$$= \vec{k}_a \prod_{R} \left[a_i^*\right]^{-\nu_i} \left[\prod_{R} \left[\frac{a_i}{a_i^*}\right]^{-\nu_i} - \prod_{P} \left[\frac{a_i}{a_i^*}\right]^{\nu_i} \right] \tag{A. 2}$$

$$\simeq \vec{k}_a \left(\prod_{R} \left[a_i^*\right]^{-\nu_i} \right) \left(\sum_{R,\, P} \frac{-\nu_i}{a_i^*} \frac{\partial a_i}{\partial \xi} \right) \left(\xi - \xi^* \right) \tag{A. 3}$$

and

$$k = \vec{k}_a \left(\prod_{R} a_i^{*\,-\nu_i} \right) \left(\sum_{R,\, P} \frac{-\nu_i}{a_i^*} \frac{\partial a_i}{\partial \xi} \right) . \tag{A. 4}$$

For an ideal solution this reduces to

$$k = \frac{\vec{k}_a}{m^*} \left(\prod_{R} y_i^{*\,-\nu_i} \right) \left(- \sum_{R,\, P} \frac{\nu_i^2}{y_i^*} + \left(\sum_{R,\, P} \nu_i \right)^2 \right) . \tag{A. 5}$$

Example II

Suppose there is a dependence of rate on concentrations which can be generally represented by:

$$\frac{d\xi}{d\theta} = \vec{k}_c \prod_{R,P,I} \left[c_i\right]^{\eta_i} - \overleftarrow{k}_c \prod_{R,P,I} \left[c_i\right]^{\lambda_i} \quad . \tag{A.6}$$

Using the relationship between $\vec{k}_c$ and $\overleftarrow{k}_c$ at equilibrium conditions

$$\frac{d\xi}{d\theta} = \vec{k}_c \prod_{R,P,I} \left[c_i^*\right]^{\eta_i} \left[\prod_{R,P,I} \left[\frac{c_i}{c_i^*}\right]^{\eta_i} - \prod_{R,P,I} \left[\frac{c_i}{c_i^*}\right]^{\lambda_i} \right] \tag{A.7}$$

$$= \vec{k}_c \prod_{R,P,I} \left[c_i^*\right]^{\eta_i} \left[\prod_{R,P,I} \left[1 + \frac{\nu_i}{m_i^*}\left(\xi - \xi^*\right)\right]^{\eta_i} - \prod_{R,P,I} \left[1 + \frac{\nu_i}{m_i^*}\left(\xi - \xi^*\right)\right]^{\lambda_i} \right] \tag{A.8}$$

$$\simeq \vec{k}_c \left(\prod_{R,P,I} \left[c_i^*\right]^{\eta_i} \right) \left(\sum_{R,P,I} \frac{\nu_i(\eta_i - \lambda_i)}{m_i^*} \right) \left(\xi - \xi^*\right) \tag{A.9}$$

and

$$k = \vec{k}_c \left(\prod_{R,P,I} \left[c_i^*\right]^{\eta_i} \right) \left(\sum_{R,P,I} \frac{\nu_i(\eta_i - \lambda_i)}{m_i^*} \right) \quad . \tag{A.10}$$

These two cases do not exhaust all possibilities. However, for any situation involving known kinetics, the k of equation (A.4) may be suitably evaluated as above in terms of a true kinetic rate constant, equilibrium concentrations (or activities), thermodynamic derivatives, and stoichiometric and kinetic coefficients.

APPENDIX B

DERIVATION OF EQUATION (51)

Consider a multiple reaction system denoting by

$$\sum_{j=1}^{n} \nu_{ij} J_j = 0 \qquad i = 1, \ldots, R \quad . \tag{B. 1}$$

The mole fraction of kth component can be expressed by

$$y_k = \frac{y_k^o + \sum\limits_{i=1}^{R} \nu_{ik} \check{\xi}_i}{1 + \sum\limits_{i=1}^{R} \sum\limits_{j=1}^{n} \nu_{ij} \check{\xi}_i} \quad . \tag{B. 2}$$

Differentiating y_k with respect to an extent of reaction, say $\check{\xi}_s$, gives

$$\left(\frac{\partial y_k}{\partial \check{\xi}_s} \right)_{T, P, \check{\xi}_\ell} = \frac{1}{Q'^2} \left\{ \nu_{sk} \cdot Q' - y_k^o \left(\sum_{j=1}^{n} \nu_{sj} \right) - \left(\sum_{j=1}^{n} \nu_{sj} \right) \left(\sum_{i=1}^{R} \nu_{ik} \check{\xi}_i \right) \right\} \tag{B. 3}$$

where

$$Q' = 1 + \sum_{i=1}^{R} \sum_{j=1}^{n} \nu_{ij} \check{\xi}_i \quad . \tag{B. 4}$$

Rearranging Eq. (B. 2) and then multiplying $\left(\sum\limits_{j=1}^{n} \nu_{sj} \right)$ to both sides of the equal sign gives

$$y_k^o\left(\sum_{j=1}^{n} \nu_{sj}\right) = y_k\left(1 + \sum_{i=1}^{R}\sum_{j=1}^{n} \nu_{ij}\,\check{\xi}_i\right)\left(\sum_{j=1}^{n} \nu_{sj}\right) - \left(\sum_{j=1}^{n} \nu_{sj}\right)\left(\sum_{i=1}^{R} \nu_{ik}\,\check{\xi}_i\right) \quad . \tag{B.5}$$

Substituting Eq. (B.5) into Eq. (B.3) and then simplifying, one obtains

$$\left(\frac{\partial y_k}{\partial \check{\xi}_s}\right)_{T,P,\check{\xi}_\ell} = \frac{1}{Q'}\left\{\nu_{sk} - y_k\left(\sum_{j=1}^{n} \nu_{sj}\right)\right\} \quad . \tag{B.6}$$

For ideal solutions

$$\ell n\, f_k = \ell n\, y_k + \ell n\, f_k^{\circledast} \tag{B.7}$$

where f_k is the fugacity of k^{th} component and the superscript, $\circledast$, denotes pure composition. Differentiating Eq. (B.7) with respect to $\check{\xi}_s$, one gets

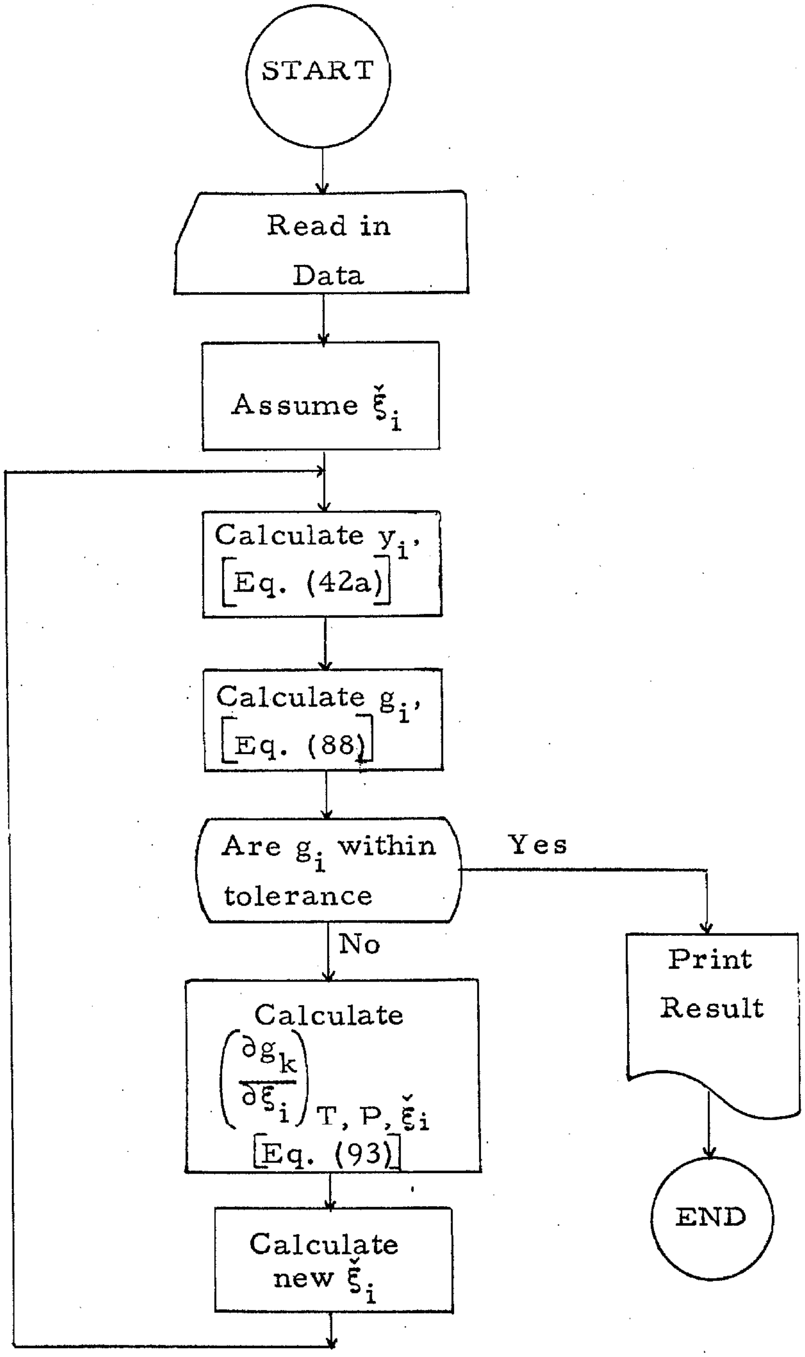
$$\left(\frac{\partial\, \ell n\, f_k}{\partial \check{\xi}_s}\right)_{T,P,\check{\xi}_\ell} = \frac{1}{y_k}\left(\frac{\partial y_k}{\partial \check{\xi}_s}\right)_{T,P,\check{\xi}_\ell} \quad . \tag{B.8}$$

Combining Eqs. (B.6) and (B.8) yields, for ideal solution,

$$\left(\frac{\partial\, \ell n\, f_k}{\partial \check{\xi}_s}\right) = \frac{1}{Q'}\left[\frac{\nu_{sk}}{y_k} - \sum_{j=1}^{n} \nu_{sj}\right] \quad . \tag{B.9}$$

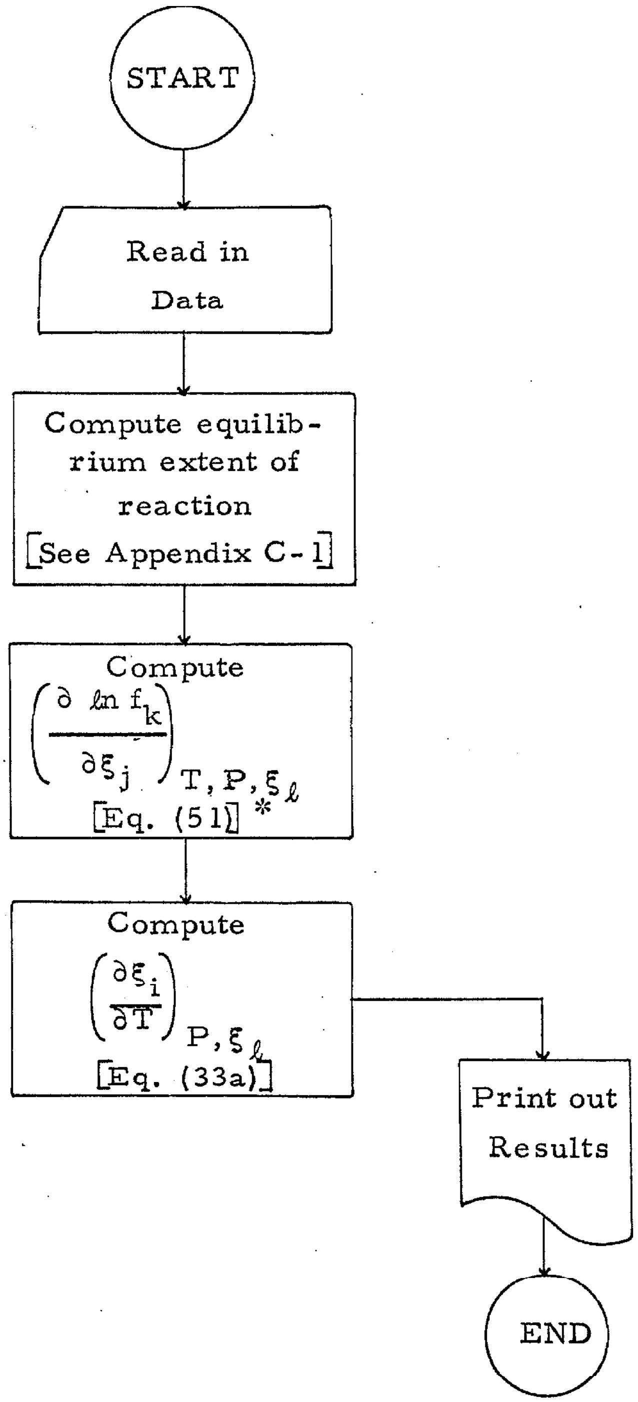
APPENDIX C-1

FLOW DIAGRAM FOR THE COMPUTATION OF EQUILIBRIUM EXTENT OF REACTION AT GIVEN TEMPERATURE AND PRESSURE



APPENDIX C-2

FLOW DIAGRAM FOR THE COMPUTATION OF $(\partial\check{\xi}_i/\partial T)_{P,\check{\xi}_\ell}$



PROPOSITIONS

PROPOSITION I

ON MEASUREMENT OF FLUID DENSITY BY A MODIFIED ROTAMETER

A variety of methods is available for measurement of fluid density. The method proposed here is to put two spherical floats of the same size but slightly different specific weight into a tapered tube.

The velocity of the fluid flowing through a Rotameter is given by

$$u = C \cdot \frac{v(\sigma_f - \sigma)}{S_f\,\sigma}^{\frac{1}{2}} \qquad (1)$$

where

u = velocity

v = volume of the float

σ = specific weight of the fluid

σ_f = specific weight of the float

S_f = maximum cross-sectional area of the float

C = constant

Let the subscripts 1 and 2 denote the two floats in the same Rotameter respectively. Since the volumetric rate of flow is the same throughout the tapered tube, we get

$$(\sigma_{f1} - \sigma)^{\frac{1}{2}}(S_1 - S_f) = (\sigma_{f2} - \sigma)^{\frac{1}{2}}(S_2 - S_f) \qquad (2)$$

where

$(S - S_f)$ = annular area between the tube wall and the float.

Now, if we adjust the flow rate such that the float 1 is at a fixed position, then

$$S_1 - S_f = \text{constant} = {\frac{1}{k}}^{\frac{1}{2}} \tag{3}$$

and

$$S_2 - S_f = F(h) \tag{4}$$

where F(h) denotes a function of the variable h, the position of the float 2. Substitute equations (3) and (4) into equation (2) and then rearrange it.

$$\sigma = \frac{kF(h)^2 \, \sigma_{f2} - \sigma_{f1}}{kF(h)^2 - 1} \quad . \tag{5}$$

The specific weight of the fluid may be calculated by equation (5).

PROPOSITION II

GENERAL EXPRESSIONS OF THERMO-ECONOMIC CRITERIA FOR OPTIMUM FEED-STOCK COMPOSITION IN GAS PHASE REACTION

In considering the closed system, gas phase reaction with no products in the feed, Prigogine and Defay(1) have shown, for a system of perfect gases, that in order to obtain the maximum yield the reactants should be combined in the ratio of their stoichiometric coefficients. Pings(2) has indicated how that result must be modified for moderately dense gases which may be described by the virial equation of state truncated at the second virial coefficient. He(3) has also pointed out that in commercial operations the maximum economic return from a reaction does not necessarily correspond to the maximum yield. Explicit expressions(3) have been derived for the distribution of initial mole fractions necessary to maximize the profit for a given distribution of values of the reactants.

The purpose of this proposition is to present a general equation for the distribution of initial mole fractions necessary to maximize the profit or the yield from a gas phase chemical reaction.

Following the analysis given by Pings(3), we may write

$$\frac{P}{m^o} = \xi \sum_{i=1}^{m} \nu_i a_i - \sum_{i=1}^{h} y_i^o \ell_i \quad . \tag{1}$$

If the feed is free from products

$$\sum_{i=1}^{h} y_i^o = 1 \quad . \tag{2}$$

At equilibrium

$$\sum_{i=1}^{m} \nu_i \, \ell n \, f_i - \frac{A^s}{RT} = 0 \tag{3}$$

where

$$f_k = y_k f_k^s \exp\left\{ \frac{P}{RT} \sum_{i=1}^{m} \sum_{j=1}^{m} y_i y_j (\Delta_{ik} + \Delta_{kj} - \Delta_{ij}) \right\} \quad . \tag{4}$$

To reduce the problem to a form suitable for mathematical analysis, let us define the following expressions.

$$g_0(y_i^o) \quad = \sum_{i=1}^{h} y_i^o - 1 = 0 \tag{5}$$

$$g_1(\xi, \, y_i^o) = \sum_{i=1}^{m} \nu_i \, \ell n \, f_i - \frac{A^{(s)}}{RT} = 0 \quad . \tag{6}$$

The equations for y_k which maximize the profit, P, then are obtained by applying the method of Lagrange's multipliers to the equations (1), (5), and (6). After a series of mathematical manipulations, we obtain

$$y_k^o = \frac{\nu_k \left\{ 1 - \check{\xi} \Omega_k / \Phi \right\} + \phi_k (1 + \check{\xi} \, \nu^{(h)}) - \nu_k \check{\xi} \, \phi^{(h)}}{\nu^{(h)} \left\{ 1 + \Omega_k / \nu^{(h)} \, \Phi \right\} + \phi^{(h)}} \tag{7}$$

where

$$\Omega_k = (1 + \check{\xi}\, \nu^{(h)})\, \ell_k - (y^o \ell)^{(h)} - \check{\xi}(\nu\ell)^{(h)} \tag{8}$$

$$\Phi = \frac{(\nu a)^{(m)}}{\theta - (\phi\beta)^{(m)}} \tag{9}$$

$$\theta = -(\nu\,\beta)^{(m)} \tag{10}$$

$$\phi_i = \frac{2p}{RT} \sum_{j=1}^{m} \left(\nu_j - y_j\, \nu^{(m)}\right) y_i \Delta_{ij} \tag{11}$$

$$\beta_i = \frac{\nu_i}{y_i^o + \nu_i \check{\xi}} - \frac{\nu^{(m)}}{1 + \nu^{(m)}\check{\xi}} \tag{12}$$

and

$$G^{(h)} = \sum_{i=1}^{h} G_i \quad . \tag{13}$$

If the gases are ideal, the second virial coefficients will be zero.

Hence

$$\Delta_{ij} = 0 \tag{14}$$

$$\phi_i = 0 \tag{15}$$

$$\Phi = (\nu a)^{(m)}/\theta \quad . \tag{16}$$

Equation (7) then reduces to

$$y_k^o = \frac{\nu_k \left\{1 - \theta\, \check{\xi}\, \Omega_k/(\nu a)^{(m)}\right\}}{\nu^{(h)} \left\{1 + \theta\, \Omega_k/\nu^{(h)}\, (\nu a)^{m}\right\}} \quad . \tag{17}$$

This is identical with the equation (15) of Pings[3]. For the non-profit case, we may assume that

$$a_i = a_i^o \, ; \qquad \ell_i = 0 \quad .$$

This leads to

$$\Omega_k = 0 \tag{18}$$

and equation (7) reduces to

$$y_k^o = \frac{\nu_k \left\{ 1 - \check{\xi} \, \phi^{(h)} + \phi_k \;\; 1 + \check{\xi} \, \nu^{(h)} \;\; / \nu_k \right\}}{\nu^{(h)} \left\{ 1 + \phi^{(h)} / \nu^{(h)} \right\}} \quad . \tag{19}$$

This expression is identical with the equation (3) of Pings[2].

Substituting equation (18) into equation (17) or equation (15) into equation (19), we obtain

$$y_k^o = \frac{\nu_k}{\nu^{(h)}} \quad . \tag{20}$$

This corresponds to the expression for the non-profit ideal gas case[1].

NOTATIONS

A^s = standard affinity of the chemical reaction (= $-\Delta F^s$).

a_i = value per mole of component i in the final equilibrium mixture.

a_i^o = value per mole of component i in the initial feed stock.

B_{ij} = contribution to the second virial coefficient arising from interaction of species i and j.

g_0 = a function defined by equation (5).

g_1 = a function defined by equation (6).

ΔF^s = standard free energy change.

f = fugacity.

h = total number of reactants.

ℓ_i = $a_i^o - a_i$, loss per mole in value of component i.

m = total number of components in system.

m^o = total number of moles in original feed stock.

P = profit.

p = pressure.

R = universal gas constant.

T = absolute temperature.

y_i^o = mole fraction of component i in original feed stock.

y_i = mole fraction of component i.

G = denotes variable.

Greek letters:

Ω = defined by equation (8).

Φ = defined by equation (9).

θ = defined by equation (10).

ϕ = defined by equation (11).

β = defined by equation (12).

ν_i = stoichiometric coefficient of component i, taking as positive for products, negative for reactants.

ξ = extent of reaction.

$\check{\xi}$ = extent of reaction per initial mole, ξ/m^o.

$\Delta_{ij} = B_{ij} - \frac{1}{2}(B_{ii} - B_{jj})$.

Superscripts:

s = denotes standard state.

o = refers to original feed stock.

(n) = indicates summation over the range 1 to n.

Subscripts:

i, k, etc. = denote components.

REFERENCES

1. Prigogine, E., R. Defay, and D. H. Everett, Chemical Thermodynamics, 134, John Wiley & Sons, Inc., New York (1962).
2. Pings, C. J., Ind. Eng. Chem. Fundamentals, 2, 244 (1963).
3. Pings, C. J., Chem. Eng. Progr., 59, No. 12, 90 (1963).

PROPOSITION III

A SYMMETRICAL FORM OF THE FOUR-SUFFIX MARGULES EQUATIONS FOR QUATERNARY SYSTEMS

ABSTRACT

The asymmetrical form of the four-suffix Margules equations for quaternary systems derived by Marek is transformed into a symmetrical form. The new form of the equations not only avoids ambiguity with the definition of the systems, but also permits easier evaluation of the activity coefficients, especially when a digital computer is used.

In the evaluation of vapor-liquid equilibrium constants of non-ideal solutions, the concept of activity is widely used. A number of equations expressing the dependence of the activity coefficients of the components on the composition of the solution have been proposed. Such relations include the Margules(2), van Laar(4, 5), Scatchard-Hamer(3), and Wohl(6) equations. Based on the concept of excess free energy of the solution, the Wohl equation assumes the most general form, from which the others can be derived according to their individual assumptions.

Although the Wohl equation for the excessive free energy is symmetrical with respect to the composition, the resulting equations for the activity coefficients are not. This not only results in possible ambiguity regarding the definition of the system, but also causes inconvenience in actual computations, particularly when a digital computer is used. Wohl(7) has presented a symmetrical form of the equations for activity coefficients of the Margules type for ternary systems. Similar forms for quaternary and higher systems are, however, not available.

Marek$^{(1)}$ has derived the four-suffix Margules equations for quaternary systems, which are not symmetrical:

$$\log \gamma_1 = \left(\frac{\partial}{\partial n_1} \frac{N \Delta G^E}{2.303\,RT}\right)_{P,\,T,\,n_2 n_3 n_4}$$

$$\begin{aligned}
&= x_2^2 \left[A_{12} + 2x_1(A_{21} - A_{12} - D_{12}) + 3x_1^2 D_{12}\right] \\
&\quad + x_3^2 \left[A_{13} + 2x_1(A_{31} - A_{13} - D_{13}) + 3x_1^2 D_{13}\right] \\
&\quad + x_4^2 \left[A_{14} + 2x_1(A_{41} - A_{14} - D_{14}) + 3x_1^2 D_{14}\right] \\
&\quad + x_2 x_3 \Big[A_{21} + A_{13} - A_{32} + 2x_1(A_{31} - A_{13}) + 2x_3(A_{32} - A_{23}) \\
&\qquad + 3x_2 x_3 D_{23} - x_1(2 - 3x_1)\, C_{1123} - x_2(1 - 3x_1)\, C_{1223} \\
&\qquad - x_3(1 - 3x_1)\, C_{1233}\Big] \\
&\quad + x_2 x_4 \Big[A_{21} + A_{14} - A_{42} + 2x_1(A_{41} - A_{14}) + 2x_4(A_{42} - A_{24}) \\
&\qquad + 3x_2 x_4 D_{24} - x_1(2 - 3x_1)\, C_{1124} - x_2(1 - 3x_1)\, C_{1224} \\
&\qquad - x_4(1 - 3x_1)\, C_{1244}\Big]
\end{aligned}$$

$$\begin{aligned}
&+ x_3x_4 \Big[A_{31} + A_{14} - A_{43} + 2x_1(A_{41} - A_{14}) + 2x_4(A_{43} - A_{34}) \\
&\qquad + 3x_3x_4\, D_{34} - x_1(2 - 3x_1)\, C_{1134} - x_3(1 - 3x_1)\, C_{1334} \\
&\qquad - x_4(1 - 3x_1)\, C_{1234}\Big] \\
&+ x_2x_3x_4 \Big[2(A_{42} - A_{24}) + 3x_2\, C_{2234} + 3x_3\, C_{2334} + 3x_4\, C_{2344} \\
&\qquad + (1 - 3x_1)\, E_{1234}\Big] \qquad (1)
\end{aligned}$$

where the various constants are given by the relations

$$A_{ij} = 2a_{ij} + 3a_{ijj} + 4a_{ijjj} \qquad (2)$$

$$D_{ij} = 4a_{iiij} + 4a_{ijjj} - 6a_{iijj} \qquad (3)$$

$$C_{iijk} = C_{ijk} + 4a_{iiij} + 4a_{iiik} - 12a_{iijk} \qquad (4)$$

$$E_{1234} = -(C_{123} + C_{124} + C_{134} + C_{234}) + 24a_{1234} \qquad (5)$$

with

$$C_{ijk} = 3a_{iij} + 3a_{ikk} + 3a_{jjk} - 6a_{ijk} + 4a_{iiij} + 4a_{ikkk} + 4a_{jjjk} \qquad (6)$$

and the restriction that in equation (6), $i < j < k$.

Similar expression for the activity coefficients of the remaining constituents can be obtained by a cyclic permutation of the indices

$$\begin{tikzcd}
1 \arrow[r] & 2 \arrow[d] \\
4 \arrow[u] & 3 \arrow[l]
\end{tikzcd}$$

Equation (1) can be rearranged, however, to a symmetrical form:

$$
\begin{aligned}
\log \gamma_1 = {} & x_2^2 \left[A_{12} + 2x_1(A_{21} - A_{12} - D_{12}) + 3x_1^2 D_{12} \right] \\
& + x_3^2 \left[A_{13} + 2x_1(A_{31} - A_{13} - D_{13}) + 3x_1^2 D_{13} \right] \\
& + x_4^2 \left[A_{14} + 2x_1(A_{41} - A_{14} - D_{14}) + 3x_1^2 D_{14} \right] \\
& + x_2 x_3 \Big[\tfrac{1}{2}(A_{21} + A_{12} + A_{31} + A_{13} - A_{32} - A_{23}) \\
& \qquad + x_1(A_{21} - A_{12} + A_{31} - A_{13} - C^*_{1123}) \\
& \qquad + (x_3 - x_2)(A_{32} - A_{23}) + 3x_2 x_3 D_{23} \\
& \qquad - (1 - 3x_1)(x_1 C^*_{1123} + x_2 C^*_{1223} + x_3 C^*_{1233}) \Big] \\
& + x_2 x_4 \Big[\tfrac{1}{2}(A_{21} + A_{12} + A_{41} + A_{14} - A_{42} - A_{24}) \\
& \qquad + x_1(A_{21} - A_{12} + A_{41} - A_{14} - C^*_{1124}) \\
& \qquad + (x_4 - x_2)(A_{42} - A_{24}) + 3x_2 x_4 D_{24} \\
& \qquad - (1 - 3x_1)(x_1 C^*_{1124} + x_2 C^*_{1224} + x_4 C^*_{1244}) \Big] \\
& + x_3 x_4 \Big[\tfrac{1}{2}(A_{31} + A_{13} + A_{41} + A_{14} - A_{43} - A_{34}) \\
& \qquad + x_1(A_{31} - A_{13} + A_{41} - A_{14} - C^*_{1134}) \\
& \qquad + (x_4 - x_3)(A_{43} - A_{34}) + 3x_3 x_4 D_{34}
\end{aligned}
$$

$$- (1 - 3x_1)(x_1 C_{1134}^* + x_3 C_{1334}^* + x_4 C_{1344}^*)\Big]$$

$$+ x_2x_3x_4\Big[3x_2 C_{2234}^* + 3x_3 C_{2334}^* + 3x_4 C_{2344}^*$$

$$+ (1 - 3x_1) E_{1234}^*\Big] \qquad (7)$$

where the constants A_{ij} and D_{ij} are the same as those defined by equations (2) and (3), and

$$C_{iijk}^* = C_{ijk}^* + 4a_{iiij} + 4a_{iiik} - 12a_{iijk} \qquad (8)$$

$$E_{1234}^* = - (C_{123}^* + C_{124}^* + C_{134}^* + C_{234}^* - 24a_{1234}) \qquad (9)$$

with

$$C_{ijk}^* = \frac{3}{2}(a_{iij} + a_{iik} + a_{ijj} + a_{jjk} + a_{ikk} + a_{jkk})$$

$$+ 2(a_{iiij} + a_{iiik} + a_{ijjj} + a_{jjjk} + a_{ikkk} + a_{jkkk})$$

$$- 6a_{ijk} \quad . \qquad (10)$$

Expressions for the activity coefficients of other components can be obtained from equation (7) by interchange of any pair of indices. For binary or ternary systems, equation (7) reduces to the forms presented by Wohl(7).

Use of equation (7) avoids the necessity of cyclic permutation and is also very convenient for machine coding.

NOTATIONS

a_{ij} = measure of interaction between molecules $i_1 j_1$ . . . etc.
A_{ij} = constants defined by equation (2).
C_{ijk} = constants defined by equation (6).
C_{ijk}^* = constants defined by equation (10).
C_{iijk} = constants defined by equation (4).
C_{iijk}^* = constants defined by equation (8).
D_{ij} = constants defined by equation (3).
E_{1234} = constants defined by equation (5).
E_{1234}^* = constants defined by equation (9).
n = total moles of a system.
n_i = moles of the ith component.
P = total pressure.
R = universal gas constant.
T = absolute temperature.
x_i = mole fraction of the i-th component.
γ_i = activity coefficient of the i-th component.
ΔG^E = excess free energy.

REFERENCES

1. Marek, J., Chem. Listy, 47, 739 (1953); Coll. Czech. Chem. Commun., 19, 1 (1954).
2. Margules, M., S. B. Akad. Wiss. Wien, Math. Naturw. Kl. II, 104, 1234 (1895).
3. Scatchard, G. and W. J. Hamer, J. Amer. Chem. Soc., 57, 1805 (1935).
4. van Laar, J. J., Z. Phys. Chem., 72, 723 (1910).
5. van Laar, J. J., Z. Phys. Chem., 185, 35 (1929).
6. Wohl, K., Trans. Amer. Inst. Chem. Eng., 42, 215 (1946).
7. Wohl, K., Chem. Eng. Progr., 49, 218 (1953).

PROPOSITION IV

EXTENDED KRASOVSKII'S METHOD FOR CONSTRUCTING THE LIAPUNOV FUNCTION

One of the basic problems associated with the study of dynamic systems is the determination of the region of stability in the state space. Due to the inherent nonlinearity of chemical kinetics, solutions to the set of differential equations describing the dynamic characteristics of chemical reactors are not available except for some special cases. Consequently, studies have been made either by linearization of the equations or by numerical techniques. Since the linearized solution provides information only in a region sufficiently close to the equilibrium point in the state space, and since enormous effort is required for the numerical technique to cover the entire region of the state space, the practical application of these methods is limited.

The direct method of Liapunov provides a way of identifying regions of stability in the state space without recourse to the solution of nonlinear differential equations. This method was proposed some seventy years ago by A. M. Liapunov(7) and became well established during the past decade mainly by contributions from Lur'e(8), Letov(6), Malkin(9), Krasovskii(2, 3), and Zubov(10). An excellent summary by Kalman and Bertram(1) and books by La Salle and Lefschetz(4) and Lefschetz(5) on this subject are available. The Liapunov technique may be summarized as follows.

Suppose that for a dynamic system

$$\underline{\dot{X}} = \underline{f}(\underline{X}) \quad \text{and} \quad \underline{f}(0) = 0 \tag{1}$$

where $\underline{X}$ is the vector of the dependent variables, $\underline{\dot{X}} = d\underline{X}/dt$, and $\underline{f}(\underline{X})$ is a vector. If there exists a region of state space within which there *exists a scalar function* $V(\underline{X})$ *with continuous first partial derivatives* such that $V(\underline{X})$ is positive definite and $\dot{V}(\underline{X})$ is negative definite, except at the origin, where $V(\underline{X}) = \dot{V}(\underline{X}) = 0$, then the system is asymptotically stable within that region. If $\dot{V}(\underline{X})$ is negative semidefinite, then the system is stable.

The major problem of applying the direct method of Liapunov to the analysis of dynamic systems is the construction of the Liapunov function, $V(\underline{X})$.

Krasovskii$^{(3)}$ has proposed an effective way of constructing the Liapunov function. For a system described by equation (1), one may assume

$$V(\underline{X}) = f^T(\underline{X})\, A\, f(\underline{X}) \tag{2}$$

where A is a positive definite symmetric matrix.

It is readily shown that the time derivative of equation (2) has the form

$$\dot{V}(\underline{X}) = f^T(\underline{X}) \left[A\, F(\underline{X}) + F^T(\underline{X})\, A \right] f(\underline{X}) \tag{3}$$

$$= -f^T(\underline{X})\, Q\, f(\underline{X}) \tag{3a}$$

where $$Q = -\left[A\,F(\underline{x}) + F^T(\underline{X})\,A\right] \tag{3b}$$

and $F(\underline{X})$ is the Jacobian matrix of the system.

Since the Liapunov function defined by equation (2) is positive definite, by applying Liapunov's theorem, one may claim that the system is asympototically stable inside the state space where $\dot{V} < 0$.

For a nonlinear system, the existance of a Liapunov function is a sufficient but not the necessary condition for the determination of stability. Hence, a point in the state space may be stable even if it is not in the region of stability defined by a particular Liapunov function. It is important to notice that the presence of the symmetric matrix A in equation (2) is very useful in constructing various Liapunov functions for a dynamic system.

In this proposition, it is suggested that the constant symmetric matrix A can be substituted by

$$A(\underline{X}) = B^T(\underline{X}) \cdot B(\underline{X}) \tag{4}$$

which is also assured to be positive definite.

Let us assume that the Liapunov function $V(\underline{X})$ has the following form.

$$V(\underline{X}) = a^T(\underline{X}) \cdot a(\underline{X}) = \sum_{\ell=1}^{n} a_\ell^2(\underline{X}) \quad . \tag{5}$$

This is a positive definite function. The time derivative of $V(\underline{X})$ is

$$\dot{V}(\underline{X}) = \sum_{i=1}^{n} \left(\frac{\partial V(\underline{X})}{\partial x_i} \right) \cdot \frac{dx_i}{dt}$$

$$= \sum_{i=1}^{n} \left(\frac{\partial V(\underline{X})}{\partial x_i} \right) f_i(\underline{X}) \quad . \tag{6}$$

Differentiating equation (5) with respect to x_i, it is obtained

$$\frac{\partial V(\underline{X})}{\partial X_i} = 2 \sum_{\ell=1}^{n} a_\ell(\underline{X}) \cdot \frac{\partial a_\ell(\underline{X})}{\partial x_i} \quad . \tag{7}$$

Substituting equation (7) into equation (6) yields

$$\dot{V}(\underline{X}) = 2 \sum_{i=1}^{n} \sum_{\ell=1}^{n} a_\ell(\underline{X}) \cdot \frac{\partial a_\ell(\underline{X})}{\partial x_i} f_i(\underline{X}) \quad . \tag{8}$$

This equation can be expressed in matrix notation as shown below.

$$\dot{V}(\underline{X}) = 2\, a^T(\underline{X}) \cdot J(\underline{X}) \cdot f(\underline{X})$$

$$= f^T(\underline{X}) \left[a^T(\underline{X}) \cdot J(\underline{X}) + J^T(\underline{X}) \cdot a(\underline{X}) \right] f(\underline{X}) \tag{9}$$

where J is an nxn matrix with elements

$$J_{ij} = \frac{\partial a_j(\underline{X})}{\partial x_i} \quad . \tag{10}$$

Now, let us introduce a matrix B such that

$$a(\underline{X}) = B(\underline{X}) \cdot f(\underline{X}) \quad . \tag{11}$$

It can readily be seen that

$$a(0) = 0 \tag{12}$$

provided $B(\underline{0})$ is bounded.

By substituting equation (11) into equation (5) it is obtained

$$V(\underline{X}) = f^T(\underline{X})\ B^T(\underline{X})\ B(\underline{X})\ f(\underline{X}) \quad . \tag{13}$$

Combining equation (13) with equation (4) gives

$$V(\underline{X}) = f^T(\underline{X})\ A(\underline{X})\ f(\underline{X}) \quad . \tag{14}$$

Since $V(\underline{X})$ is a positive definite function and $V(\underline{0}) = 0$, it is a legitimate Liapunov function for the dynamic system represented by equation (1). It follows immediately that the system is asymptotically stable inside the region where the matrix

$$-Q = B^T(\underline{X}) \cdot J(\underline{X}) + J^T(\underline{X})\ B(\underline{X}) \tag{15}$$

is positive definite.

As a special case, let us assume that the matrix B in equation (11) is a constant matrix. Hence, by expanding equation (11) one gets

$$a_j(\underline{X}) = \sum_{k=1}^{n} \beta_{jk}\ f_k(\underline{X}) \quad . \tag{16}$$

By differentiating it with respect to x_i it is obtained

$$J_{ij} = \frac{\partial a_j(\underline{X})}{\partial x_i} = \sum_{k=1}^{n} \beta_{jk} \frac{\partial f_k(\underline{X})}{\partial x_i} \tag{17}$$

or

$$J(\underline{X}) = B\ F(\underline{X}) \tag{18}$$

where F is the Jacobian matrix of the system.

Combining equations (4), (15), and (18) it is obtained

$$\begin{aligned} -Q &= B^TB\ F(\underline{X}) + F^T(\underline{X})\ B^TB \\ &= A\ F(\underline{X}) + F^T(\underline{X})\ A \quad . \end{aligned} \tag{19}$$

It can readily be pointed out that equation (19) and equation (3b) are identical.

REFERENCES

1. Kalman, R. E., and J. E. Bertran, *Trans. ASME Series D.*, *82*, 371 (1960).
2. Krasovskii, N. N., *P.M.M.*, *18*, 735 (1954), in Russian.
3. Krasovskii, N. N., "Stability of Motion," translated by J. L. Brenner, Stanford University Press (1963).
4. LaSalle, J., and S. Lefschetz, *Stability by Liapunov's Direct Method with Applications*, Academic Press, New York, N. Y. (1961).
5. Lefschetz, S., *Stability of Nonlinear Control System*, Academic Press, New York, N. Y. (1965).
6. Letov, A. M., *Stability in Nonlinear Control System*, Princeton University Press (1961).
7. Liapunov, M. A., "Probleme general de la stabilite du mouvement. Annals of mathematics studies," No. 17, Princeton University Press (1947). (Translation of the original publication in "The Communications of the Mathematics Society of Kharkow.")
8. Lur'e, A. I., *Some Nonlinear Problems in the Theory of Automatic Control*, Grostekhizdat, Moscow (1951). English translation: Her Majesty's Stationary Office, London (1957).
9. Malkin, I. G., "Theory of Stability of Motion," AEC Translation No. 3352, Dept. of Commerce, Washington, D.C. (1958).
10. Zubov, V. I., "Methods of A. M. Liapunov and Their Application," AEC-tr-4439, Office of Technical Services, Department of Commerce, Washington, D. C.

PROPOSITION V

ON THE STABILITY CRITERION OF MULTIPLE REACTION SYSTEM UNDER ISOTHERMAL-ISOBARIC CONDITION

Prigogine and Defay(2) have developed a stability condition using the second law of thermodynamics for systems where R simultaneous reactions can take place. They have also shown that the condition is always satisfied in an ideal system, so that equilibria in ideal systems are always stable. However, the condition of the existance of more than one equilibrium point in a chemically reacting system is not found. Nor is a real example available.

It is hoped that by numerically computing the free energy of a multiple reaction system at constant temperature and pressure as a function of extent of reactions, a better understanding of this problem may be obtained.

One way of obtaining the free energy of a system is by using the equation of state. For simplicity, the virial equation of state truncated up to the second term is used.

$$\frac{PV}{RT} = 1 + B(T)/V \quad . \qquad (1)$$

The free energy function corresponding to this equation of state is given by the following equation(6).

$$\frac{F - F^o}{RT} = \frac{1}{V}\left[B - T\frac{dB}{dT}\right] + \ln p + \frac{T}{V}\frac{dB}{dT} + \frac{B^2}{2V^2} \qquad (2)$$

B denotes the second virial coefficient of the system and may be computed from the following combination rule(6).

$$B = \sum_i \sum_j y_i\, y_j\, B_{ij} \quad . \tag{3}$$

The mole fraction of a multiple reaction system can be expressed as

$$y_j = \frac{y_j^o + \sum_i \nu_{ij}\, \xi_i}{1 + \sum_i \sum_\ell \nu_{i\ell}\, \xi_i} \tag{4}$$

where ν_{ij} is the stoichiometric coefficient of j^{th} component in i^{th} reaction. ξ_i is the extent of reaction of i^{th} reaction. y_j^o is the initial mole fraction of j^{th} component. It can be seen that by substituting equations (1), (3), and (4) into equation (2) the free energy function, $(F - F^o)/RT$, may be expressed as a function of extent of reactions.

The steam-methane reaction is chosen as an example. The chemical reactions involved are:

$$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2 \tag{R-1}$$

$$CH_4 + 2\,H_2O \rightleftharpoons CO_2 + 4\,H_2 \tag{R-2}$$

Values of the free energy function are computed for different combinations of extent of reactions at 300°C and 30 atm. with initial mole fraction of $y^o_{CH_4} = 0.5$ and $y^o_{H_2O} = 0.5$. The result is given in Table I. Since the free energy function increases monotonously with the increase in extent of reaction, the contour of the total free energy in the state space will not be changed by the correction due to the deviation from the ideal mixture.

Also this experiment does not give a definite answer to the question regarding the existance of more than one equilibrium point in a multiple reaction system at isothermal-isobaric condition. It is hoped that it has presented the problem in a more concrete manner and also has pointed out one possible way of studying the problem.

Now, let us proceed one step further and ask ourselves the following question. Suppose there exist more than one equilibrium point in a multiple reaction system, can we identify which one is stable and which one is unstable? This question can be answered by means of the second method of Liapunov.

Suppose that there exists an equilibrium state, denoted by I, for a multiple reaction system characterized by the following set of chemical reactions

$$\sum_{j=1}^{n} \nu_{ij} B_j = 0 , \qquad i = 1,\ldots,R \tag{5}$$

where B_j is the chemical symbol of the j^{th} component and ν_{ij} is the stoichiometric coefficient of the j^{th} component in the i^{th} reaction taken as positive for products, negative for reactants, and zero for component not participating in the reaction. At the vicinity of the equilibrium state the rate of reaction, $\dot{\xi}$, can be expressed as(1)

$$\dot{\xi}_i = \sum_{j=1}^{R} \ell_{ij} A_j , \qquad i = 1,\ldots,R \tag{6}$$

where A_j is the affinity of the j^{th} reaction and ℓ_{ij} is the Onsager phenomenological coefficient for the j^{th} component in the i^{th} reaction. Expanding the affinity under isothermal-isobaric condition gives

$$A_j = A_j^* + \sum_{k=1}^{R} \left(\frac{\partial A_j}{\partial \xi_k}\right)^*_{T,P,\xi_\ell} \left(\xi_k - \xi_k^*\right)$$

$$+ \cdots \tag{7}$$

where the superscript * denotes equilibrium state. Since the affinity of an equilibrium state is zero$^{(2)}$, by truncating the higher order terms equation (7) becomes

$$A_j = \sum_{k=1}^{R} \left(\frac{\partial A_j}{\partial \xi_k}\right)^*_{T,P,\xi_\ell} \left(\xi_k - \xi_k^*\right) \quad . \tag{8}$$

By combining equations (6) and (8) it is obtained

$$\dot{\xi}_i = \sum_{k=1}^{R} \sum_{j=1}^{R} \ell_{ij} \left(\frac{\partial A_j}{\partial \xi_k}\right)^*_{T,P,\xi_\ell} \left(\xi_k - \xi_k^*\right) \quad , \qquad i = 1, \ldots, R \quad . \tag{9}$$

Equation (9) is the set of differential equations governing the changes of extent of reaction with respect to time. The stability criteria of it can readily be obtained by using the direct method of Liapunov. The direct method of Liapunov is summarized as follows$^{(3-5)}$.

Suppose that for a dynamic system

$$\dot{\underline{X}} = \underline{f}(\underline{X}) \quad \text{and} \quad \underline{f}(0) = 0 \tag{10}$$

where $\underline{X}$ is the vector of dependent variables, $\dot{\underline{X}} = d\underline{X}/dt$, and $\underline{f}(\underline{X})$ is a vector. If there exists a region of state space within which there exists a scalar function $V(\underline{X})$ with continuous first partial derivatives such that $V(\underline{X})$ is positive definite and $\dot{V}(\underline{X})$ is negative definite, except at the origin, where $V(\underline{X}) = \dot{V}(\underline{X}) = 0$, then the system is asymptotically stable within that region. If $\dot{V}(\underline{X})$ is negative semidefinite, then the system is stable.

The major problem of applying the direct method of Liapunov to the analysis of dynamic systems is the construction of the Liapunov function, $V(\underline{X})$.

Krasovskii$^{(3)}$ has proposed an effective way of constructing the Liapunov function. For a system described by equation (10) one may assume

$$V(\underline{X}) = f^T(\underline{X})\, D\, f(\underline{X}) \tag{11}$$

where D is a positive definite symmetric matrix.

It can readily be shown that the time derivative of equation (11) has the form

$$\dot{V}(\underline{X}) = f^T(\underline{X}) \left[D\, F(\underline{X}) + F^T(\underline{X})\, D \right] f(\underline{X}) \tag{12}$$

$$= -f^T(\underline{X})\; Q\; f(\underline{X}) \tag{13}$$

where

$$Q = -\left[D\, F(\underline{x}) + F^T(\underline{X})\, D \right] \tag{14}$$

and $F(\underline{X})$ is the Jacobian matrix of the system.

Since the Liapunov function defined by equation (11) is positive definite, by applying Liapunov's theoren, one may claim that the system is asymptotically stable inside the state space where $Q > 0$.

In order to apply the direct method of Liapunov the system equation, equation (9), must be transformed such that the equilibrium point is also the origin of the state space. This can be done by letting

$$\hat{\xi} = \xi_k - \xi_k^* \quad . \tag{15}$$

Equation (9) then becomes

$$\dot{\hat{\xi}}_i = \sum_{k=1}^{R} \sum_{j=1}^{R} \ell_{ij} \left(\frac{\partial A_j}{\partial \hat{\xi}_k} \right)^*_{T,P,\xi_\ell} \hat{\xi}_k \ , \qquad i = 1, \ldots, R \quad . \tag{16}$$

It must be pointed out that the criteria of stability obtained by way of the direct method of Liapunov are sufficient, but not necessary conditions.

Krasovskii's method is used for the construction of the Liapunov function.

By letting the constant matrix D in equation (11) be equal to unit matrix it is obtained

$$V(\hat{\xi}) = \sum_{i=1}^{R} \left\{ \sum_{k=1}^{R} \sum_{j=1}^{R} \ell_{ij} \left(\frac{\partial A_j}{\partial \hat{\xi}_k} \right)_{T,P,\xi_\ell} \hat{\xi}_k \right\}^2 \quad . \tag{17}$$

It follows immediately that

$$Q_{ik} = - \sum_{j=1}^{R} \left\{ \ell_{ij} \left(\frac{\partial A_j}{\partial \hat{\xi}_k} \right)_{T,P,\xi_\ell} + \ell_{kj} \left(\frac{\partial A_j}{\partial \hat{\xi}_i} \right)_{T,P,\xi_\ell} \right\} \tag{18}$$

where Q_{ik} is an element at the i^{th} row and k^{th} column of matrix Q. The stability criterion becomes

$$Q > 0 \quad . \tag{19}$$

REFERENCES

1. Pings, C. J., and E. B. Nebeker, I&EC Fundamentals, 4, 376-381 (1965).
2. Prigogine, I., and R. Defay, Chemical Thermodynamics, Longmans, Green, New York (1954).
3. Krasovskii, N. N., "Stability of Motion," translated by J. L. Brenner, Stanford University Press (1963).
4. Kalman, R. E., and J. E. Bertram, Trans. ASME Series D., 82, 371 (1960).
5. LaSalle, J., and S. Lefschetz, Stability by Liapunov's Direct Method with Applications, Academic Press, New York, N. Y. (1961).
6. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York, N. Y. (1954).

TABLE I

THE FREE ENERGY FUNCTION (F-F°)/RT FOR THE REACTION SYSTEM

$CH_4 + H_2O \rightleftharpoons 3\,H_2 + CO$ (R-1)

$CH_4 + 2\,H_2O \rightleftharpoons 4\,H_2 + CO_2$ (R-2)

AT T = 300°C AND P = 30 ATM.

ξ_2 \ ξ_1	0.0	0.1	0.2
0.02	3.385	3.399	3.406
0.04	3.391	3.402	3.408
0.06	3.395	3.404	3.409
0.08	3.398	3.406	3.410
0.10	3.401	3.408	3.411
0.12	3.404	3.409	3.411
0.14	3.406	3.410	3.412
0.16	3.407	3.411	
0.18	3.408	3.411	
0.20	3.409	3.412	
0.22	3.410		
0.24	3.411		