The Control of Nonlinear Systems.

Part III: Invariant Imbedding and Quasilinearization

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An iterative technique is proposed that solves the two-point boundary value problem formed from the variational equations for the optimal control of nonlinear systems. The computational algorithm utilizes invariant imbedding to provide a set of the unknown boundary conditions and quasilinearization to calculate the optimal control policy. A numerical example indicates that the method exhibits considerable promise.

It is well known that the variational equations for the optimal control of an n dimensional dynamic system form a two-point boundary value problem. There usually exist $2n$ differential equations with n boundary conditions prescribed at the initial time of control and n boundary conditions prescribed at the final time of control. To solve these variational equations one may ignore the unknown n boundary conditions at each end of the control sequence (*5, 7*), or one may try to determine an explicit set of these boundary conditions. In the latter case once the unknown boundary conditions are determined the problem can, in theory at least, be thought of as solved.

In the present paper an iterative technique is outlined which uses invariant imbedding (*1, 10*) to define a set of the unknown boundary conditions and then combines this with quasilinearization (*6, 8, 10*) to determine the optimal control. As shown by numerical example, the method exhibits considerable promise for solving nonlinear chemical engineering control problems.

THE VARIATIONAL EQUATIONS

Consider the continuous nonlinear system

$$\dot{\mathbf{x}}(t) = \mathbf{f}(\mathbf{x}, \mathbf{u}, t), \quad 0 \leq t \leq t_f \tag{1}$$

where $\mathbf{x}$ is an n dimensional state vector, $\mathbf{u}$ an r dimensional decision or control vector, and t a time variable. If the initial state of the system is prescribed as

$$\mathbf{x}(0) = \mathbf{x}^o \tag{2}$$

and it is desired to maximize the generalized final-value performance index

$$I[\mathbf{x}(t_f)] \tag{3}$$

by the choice of $\mathbf{u}(t)$, then Pontryagin's maximum principle (9) provides necessary conditions for the optimality of I. Namely, if we define a Hamiltonian function

$$H(\mathbf{x}, \mathbf{u}, \mathbf{z}, t) = \sum_{i=1}^{n} z_i \dot{x}_i \tag{4}$$

and an adjoint vector $\mathbf{z}$ by

$$\dot{z}_i = -\frac{\partial H}{\partial x_i}, \qquad i = 1, \ldots, n \tag{5}$$

with final values prescribed as

$$z_i(t_f) = \frac{\partial I}{\partial x_i}\bigg|_{t=t_f} \qquad i = 1, \ldots, n \tag{6}$$

then $\mathbf{u}(t)$ is optimal if it maximizes H. Note that in the Hamiltonian nomenclature Equation (1) can be written as

$$\dot{x}_i = \frac{\partial H}{\partial z_i}, \; i = 1, \ldots, n \tag{7}$$

Thus we have n differential equations, Equation (7), with n initial values, Equation (2). Coupled with these state equations are n differential equations, Equations (5), with n final values specified by Equation (6). This forms the two-point boundary value problem with the initial adjoint conditions $\mathbf{z}(0)$ and the final state values $\mathbf{x}(t_f)$ unknown.

INVARIANT IMBEDDING

In this paper we propose a technique which makes use of the method of invariant imbedding (*1, 10*). This method characteristically has been used to replace two-point boundary value problems arising in classical transport problems by equivalent initial value problems.

To illustrate the application of invariant imbedding to the optimal control problem, rewrite Equations (1) to (6) as

$$\dot{\mathbf{x}}(t) = \mathbf{f}(\mathbf{x}, \mathbf{z}, t) \qquad 0 \leq t \leq t_f \tag{8}$$

$$\dot{\mathbf{z}}(t) = \mathbf{g}(\mathbf{x}, \mathbf{z}, t) \tag{9}$$

with

$$\mathbf{x}(0) = \mathbf{x}^o \tag{10}$$

$$\mathbf{z}(t_f) = \mathbf{z}^f \tag{11}$$

We have assumed that the maximization of H yields $\mathbf{u}(t)$ as a function of $\mathbf{x}(t)$ and $\mathbf{z}(t)$, and this allows $\mathbf{u}(t)$ to be eliminated from Equations (1) and (5). Define

$$R_i(\mathbf{x}^o, t_o) = z_i(t_o), \qquad i = 1, 2, \ldots, n \tag{12}$$

where t_o is a general initial time, and consider $\mathbf{z}(t_o + \Delta)$ where Δ is a differential increment in the initial time t_o. From Equation (9) we get

$$\mathbf{z}(t_o + \Delta) = \mathbf{R}(\mathbf{x}^o, t_o) + \Delta \mathbf{g}[\mathbf{x}^o, \mathbf{R}(\mathbf{x}^o, t_o), t_o] + o(\Delta) \tag{13}$$

But from Equation (8) and the definition of $\mathbf{R}$, the following expression for $\mathbf{z}(t_o + \Delta)$ may also be obtained:

$$\mathbf{z}(t_o + \Delta) = \mathbf{R}[\mathbf{x}^o + \Delta \mathbf{f}\{\mathbf{x}^o, \mathbf{R}(\mathbf{x}^o, t_o) t_o\}, t_o + \Delta] + o(\Delta) \tag{14}$$

Equating Equations (13) and (14) one gets

$$\frac{1}{\Delta}[\mathbf{R}\{\mathbf{x}^o + \Delta \mathbf{f}\{\mathbf{x}^o, \mathbf{R}(\mathbf{x}^o, t_o), t_o\}, t_o + \Delta\} - \mathbf{R}(\mathbf{x}^o, t_o)] = \mathbf{g}[\mathbf{x}^o, \mathbf{R}(\mathbf{x}^o, t_o), t_o] + o(\Delta) \tag{15}$$

Taking the limit of Equation (15) as $\Delta \to 0$ one obtains

$$\frac{d\mathbf{R}}{dt_o} = \mathbf{g}(\mathbf{x}^o, \mathbf{R}, t_o) \tag{16}$$

But

$$\frac{d\mathbf{R}}{dt_o} = \frac{\partial \mathbf{R}}{\partial t_o} + \sum_{j=1}^{n} f_j(\mathbf{x}^o, \mathbf{R}, t_o) \frac{\partial \mathbf{R}}{\partial x_j{}^o} \tag{17}$$

and a combination of Equations (16) and (17) results in the following set of n partial differential equations

$$\frac{\partial R_i}{\partial t_o} + \sum_{j=1}^{n} f_j(\mathbf{x}^o, \mathbf{R}, t_o) \frac{\partial R_i}{\partial x_j{}^o} = g_j(\mathbf{x}^o, \mathbf{R}, t_o) \tag{18}$$

with final values

$$R_i(\mathbf{x}^o, t_f) = z_i{}^f, \quad i = 1, 2, \ldots, n \tag{19}$$

Equation (18), with the final condition of Equation (19), gives the dependence of the initial value of $\mathbf{z}$ on the initial value of $\mathbf{x}$ and the initial value of the independent variable t for a given final value of $\mathbf{z}$. Once the solution to Equations (18) and (19) is in hand, Equations (8) and (9) are reduced to an initial value problem.

This development could just as easily yielded the missing final conditions on $\mathbf{x}$ instead of the missing initial condition on $\mathbf{z}$. The crux of the use of the method lies in the solution of Equation (18), a point to be shortly considered further. However, it is obvious that the solution may be most difficult, if not impossible, unless numerical procedures are used.

INVARIANT IMBEDDING APPLIED TO THE BASIC QUASILINEARIZATION ALGORITHM

Since the overall procedure we shall use is an iterative one, we assume for the moment that we have computed the k^{th} approximation to the optimal values of $\mathbf{x}(t)$ and $\mathbf{z}(t)$. Denoting this by $\mathbf{x}^{(k)}(t)$ and $\mathbf{z}^{(k)}(t)$ and linearizing Equations (8) and (9) for the $(k+1)^{\text{th}}$ approximation about the k^{th} approximation we get

$$\dot{\mathbf{x}}^{(k+1)} = \mathbf{f}(\mathbf{x}^{(k)}, \mathbf{z}^{(k)}, t) + \frac{\partial \mathbf{f}}{\partial \mathbf{x}} \delta\mathbf{x} + \frac{\partial \mathbf{f}}{\partial \mathbf{z}} \delta\mathbf{z} \tag{20}$$

$$\dot{\mathbf{z}}^{(k+1)} = \mathbf{g}(\mathbf{x}^{(k)}, \mathbf{z}^{(k)}, t) + \frac{\partial \mathbf{g}}{\partial \mathbf{x}} \delta\mathbf{x} + \frac{\partial \mathbf{g}}{\partial \mathbf{z}} \delta\mathbf{z} \tag{21}$$

where $\delta\mathbf{x} = \mathbf{x}^{(k+1)} - \mathbf{x}^{(k)}$ and $\delta\mathbf{z} = \mathbf{z}^{(k+1)} - \mathbf{z}^{(k)}$. The Jacobian matrices $\partial\mathbf{f}/\partial\mathbf{x}$, $\partial\mathbf{f}/\partial\mathbf{z}$, $\partial\mathbf{g}/\partial\mathbf{x}$, and $\partial\mathbf{g}/\partial\mathbf{z}$ are evaluated at the k^{th} approximation. Note that Equations (20) and (21) are linear in the $(k+1)^{\text{th}}$ approximation. This nonlinear boundary value problem can obviously be solved more easily than the original nonlinear one given by Equations (8) to (11). Further, we shall require that the solution to Equations (20) and (21) satisfy the known boundary conditions given by Equations (10) and (11). The general iterative technique which uses the linear system of equations is known as *quasilinearization (10)* or the *Newton-Raphson algorithm (8)*. Kalaba (4) has shown that under certain conditions convergence of the sequence $\{\mathbf{x}^{(k)}, \mathbf{z}^{(k)}\}$ is not only monotonic, but quadratic.

To solve this new linear boundary value problem we shall apply invariant imbedding to find the missing initial conditions on $\mathbf{z}^{(k+1)}$. To simplify the nomenclature, write Equations (20) and (21) as

$$\dot{x}_i{}^{(k+1)} = \sum_{j=1}^{n} [t_{ij} x_j{}^{(k+1)} + \tau_{ij} z_j{}^{(k+1)}] + t_i \tag{22}$$

$$\dot{z}_i{}^{(k+1)} = \sum_{j=1}^{n} [s_{ij} x_j{}^{(k+1)} + \sigma_{ij} z_j{}^{(k+1)}] + s_i \tag{23}$$

where

$$t_{ij} = \frac{\partial f_i}{\partial x_j}, \tau_{ij} = \frac{\partial f_i}{\partial z_j}, s_{ij} = \frac{\partial g_i}{\partial x_j}, \sigma_{ij} = \frac{\partial g_i}{\partial z_j}$$

and t_i and s_i represent the inhomogeneous parts of Equations (20) and (21), respectively.

As before, let $\mathbf{R}(\mathbf{x}^o, t_o) \equiv \mathbf{z}(t_o)$. Then Equation (18) becomes

$$\frac{\partial R_i}{\partial t_o} + \sum_{j=1}^{n} \left[\sum_{k=1}^{n} (t_{jk} x_k{}^o + \tau_{jk} R_k) + t_j \right] \frac{\partial R_i}{\partial x_j{}^o} = \sum_{k=1}^{n} (s_{ik} x_k{}^o + \sigma_{ik} R_k) + s_i \tag{24}$$

In this case the solution to Equation (19) will be of the form

$$R_i(\mathbf{x}^o, t_o) = \sum_{k=1}^{n} x_k{}^o M_{ik}(t_o) + N_i(t_o) \tag{25}$$

Substituting Equation (25) into Equation (24) and collecting terms in $x_k{}^o$, we arrive at the following set of $n(n+1)$ ordinary differential equations:

$$\frac{dM_{ik}}{dt_o} = s_{ik} + \sum_{j=1}^{n} \sigma_{ij} M_{jk} - \sum_{j=1}^{n} \left(t_{jk} + \sum_{l=1}^{n} \tau_{jl} M_{lk} \right) M_{ij}, \; i, k = 1, 2, \ldots, n \tag{26}$$

$$\frac{dN_i}{dt_o} = s_i + \sum_{k=1}^{n} \sigma_{ik} N_k - \sum_{j=1}^{n} \left(t_j + \sum_{k=1}^{n} \tau_{jk} N_k \right) M_{ij}, \; i = 1, 2, \ldots, n \tag{27}$$

The final values for Equations (26) and (27) become, from Equations (19) and (25)

$$M_{ik}(t_f) = 0 \tag{28}$$

and

$$N_i(t_f) = z_i{}^f \tag{29}$$

Now we are in a position to define the overall iterative algorithm which uses the combination of invariant imbedding and quasilinearization to generate the optimal control function. This algorithm may be stated as follows:

1. Assume $\mathbf{x}^{(0)}(t)$ and $\mathbf{z}^{(0)}(t)$.
2. Integrate Equations (26) and (27) from $t = t_f$ to $t = 0$ with final values given by Equations (28) and (29).
3. Find the missing initial conditions for $\mathbf{z}^{(k+1)}$ from Equation (25) using the given values of $x_k{}^o$ along with M_{ik} and N_i from step 2.
4. Integrate Equations (20) and (21) from $t = 0$ to $t = t_f$ to generate $\mathbf{x}^{(k+1)}(t)$ and $\mathbf{z}^{(k+1)}(t)$.
5. If the $(k+1)^{\text{th}}$ and k^{th} approximations are within a certain desired tolerance, the iteration is stopped. Otherwise repeat to step 2.

Incorporating invariant imbedding provides a way of avoiding certain difficulties encountered in the usual quasilinearization algorithm outlined in references 8 and 10. The normal procedure is to generate a series of homogeneous solutions and a particular solution to Equations (17) and (18) and to form a linear combination of these solutions by the superposition principle. The weighting constants in the linear combination are chosen to satisfy the n initial conditions and the n final conditions given by Equations (10) and (11). Solving for these weighting constants requires the solution of a system of linear, algebraic

equations. This often causes numerical difficulties due to the necessity of matrix inversion. The use of invariant imbedding replaces superposition and in this way bypasses the potentially troublesome solution of linear, algebraic equations.

It has already been pointed out that employing invariant imbedding to calculate the missing boundary conditions on the nonlinear differential equations yields a nonlinear set of partial differential equations. By linearizing Equations (8) and (9) and then using invariant imbedding to solve the resulting linear boundary value system, we simplify the invariant imbedding equations. However, the solution of the linear problem by this method is obviously only an approximation to the solution of the original nonlinear problem. Iteration is therefore necessary to obtain the desired optimal solution; this is obtained as the limit of a sequence of solutions, each one of which is the solution to a linear boundary value problem. Thus the invariant imbedding quasilinearization algorithm combines the best features of the individual methods. It is, however, difficult to place the combined method within the classification of Dreyfus (3).

To summarize, quasilinearization approximates the nonlinear boundary value problem by a linear one. Invariant imbedding then transforms this linear boundary value problem into an initial value one by determining the missing initial conditions.

THE METHOD OF GREEN'S FUNCTIONS

To put the current method into proper perspective it is of interest to detail an alternate procedure for solving the same problem as advocated by Denn and Aris (2). They propose the following iterative scheme for solving the two-point boundary value problem posed by Equations (1), (2), (5), and (6).

1. Assume a value of $\mathbf{x}(t_f)$ (note that the boundary condition is selected here).
2. Integrate Equations (1) and (5) from $t = t_f$ to $t = 0$, where the final values of $\mathbf{z}$ are given by Equation (6) and $\mathbf{u}(t)$ is chosen to maximize H. If the calculated $\mathbf{x}(0)$ equals $\mathbf{x}^o$, the calculation is completed; otherwise proceed to the next step.
3. Integrate the adjoint differential equation for the linearized state equation, namely

$$\dot{z}_i^k = -\sum_{j=1}^{n} \frac{\partial f_j}{\partial x_i} z_j^k, \quad i, k = 1, \ldots, n \tag{30}$$

n times from $t = t_f$ to $t = 0$ with final values

$$z_i^k(t_f) = \delta_i^k \tag{31}$$

where δ_i^k is Kronecker's delta, equaling 1 if $i = k$ and zero otherwise. This step generates the so-called Green's tensor of Denn and Aris, composed of the n vectors $\mathbf{z}^k(t)$.
4. From the Green's tensor calculate a new approximation to $\mathbf{x}(t_f)$ from

$$x_i^{\text{new}}(t_f) = x_i^{\text{old}}(t_f) + \frac{1}{\lambda} \sum_{j=1}^{n} z_j^i(0)\,[x_j^o - x_j(0)] \tag{32}$$

where λ is a constant greater than unity which is adjusted as the iteration proceeds to reduce oscillations. In Equation (32) $\mathbf{x}(0)$ is the initial state vector calculated in step 2 and $\mathbf{x}^{\text{old}}(t_f)$ is the previous value of $\mathbf{x}(t_f)$.
5. Return to step 2.

Note that in the method outlined above Equations (1), (5), and (6) are satisfied at each iteration. In addition $\mathbf{u}(t)$ is the optimal control for the particular value of $\mathbf{x}(0)$ which results from step 2. The unsatisfied condition is the initial state given by Equation (2) and successive iteration attempts to meet this requirement. This algorithm falls in the class of techniques called *successive approximation to the problem* by Dreyfus (3).

Invariant imbedding used with quasilinearization performs much the same function as the Green's tensor does in the method of Green's functions outlined above. Both provide a way of improving on the value of a missing boundary condition based on the results of the previous iteration. Notice, however, that quasilinearization satisfies all of the known boundary conditions and the optimality of $\mathbf{u}$ at each iteration.

Quasilinearization, with invariant imbedding on the linearized equations, requires the storage of the k^{th} approximation and the integration of $n(n+3)$ equations at each iteration. The method of Green's functions also requires the storage of the k^{th} approximation, but the integration of only $n(n+2)$ equations. If more storage is available, Green's tensor may be stored as well so that only $n(n+1)$ equations must be integrated at each iteration (2). In practice, the computing equipment needed to implement both algorithms is almost equivalent.

A NUMERICAL EXAMPLE

The following problem demonstrates the invariant imbedding quasilinearization algorithm. The system described below has been used by Denn and Aris (2) and Wang and Fan (11) in equivalent or slightly revised form.

The first-order reactions $A \rightarrow B \rightarrow C$ are carried out in a tubular reactor. It is desired to maximize the outlet concentration of the intermediate by the choice of the temperature profile. The state equations for this system are

$$\frac{dx_1}{dt} = -k_1 x_1 \tag{33}$$

$$\frac{dx_2}{dt} = k_1 x_1 - k_2 x_2 \tag{34}$$

where

$$k_i = G_i\, e^{-E_i/RT}, \quad i = 1, 2 \tag{35}$$

The initial state of the system is

$$x_1(0) = x_1^o \tag{36}$$

$$x_2(0) = x_2^o \tag{37}$$

When one follows the maximum principle

$$H = -z_1 k_1 x_1 + z_2(k_1 x_1 - k_2 x_2) \tag{38}$$

and

$$\frac{dz_1}{dt} = k_1(z_1 - z_2) \tag{39}$$

$$\frac{dz_2}{dt} = k_2 z_2 \tag{40}$$

with

$$z_1(t_f) = 0 \tag{41}$$

$$z_2(t_f) = 1 \tag{42}$$

Maximizing H by the choice of $T(t)$ one gets

$$T(t) = \frac{(E_1 - E_2)/R}{\ln\left[\dfrac{E_1 G_1 x_1(z_2 - z_1)}{E_2 G_2 x_2 z_2}\right]} \tag{43}$$

Substituting Equation (43) into Equation (35) and the result into Equations (33), (34), (39), and (40) one gets the state and adjoint equations in the form of Equations (8) and (9).

The invariant imbedding quasilinearization algorithm was programmed for an IBM 7094 computer with the

TABLE 1. MODEL PARAMETERS

$E_1 = 18{,}000$ cal./mole
$E_2 = 30{,}000$ cal./mole
$R = 1.987$ cal./(mole)(°K.)
$G_1 = 5.35 \times 10^{10}$ min.$^{-1}$
$G_2 = 4.61 \times 10^{17}$ min.$^{-1}$
$t_f = 8$ min.
$x_1^o = 0.53$ mole fraction
$x_2^o = 0.43$ mole fraction

parameters of Table 1. In Tables 2 and 3 are shown certain selected runs with different starting values of $z_1^{(0)}(0)$, and $z_2^{(0)}(0)$. In each case the iteration was assumed to have converged when the maximum difference between the state and adjoint trajectories for the k^{th} and $(k+1)^{\text{th}}$ approximations was less than $\pm 10^{-3}$. A Runge-Kutta-Gill routine was used to integrate the differential equations. In both cases the final values of $x_1(t_f)$ and $x_2(t_f)$ were 0.1704 and 0.6794, respectively, with the temperature profile decreasing from 343°K. at the reactor inlet to 338°K. at the outlet.

As can be seen the algorithm converges rapidly but is a mild function of the initial guess on the $\mathbf{z}^{(0)}(0)$. In Table 2 the initial guess is close to the correct optimal values of $z_1(0) = -0.61000$ and $z_2(0) = -0.82824$; in Table 3 the initial guess is quite far from the optimal values. In both cases convergence occurred rather rapidly. While not evident from these results, as $\mathbf{z}^{(0)}(0)$ deviated more and more from the true optimum values, numerical accuracy in the computation became more important. Because of this feature Table 3 required a much smaller numerical integration step size.

CONCLUSIONS

It is impossible to make a universal statement regarding the general applicability of the invariant imbedding quasilinearization algorithm, or any other method, for that matter. However, certain statements can be made on the basis of our experience with the method.

1. The algorithm requires only a small amount of computer storage so that multidimensional systems can be handled.

2. As with all iterative techniques a good assumption for the starting point in the successive approximation algorithm helps to assure convergence.

3. In general convergence is quite fast.

4. Quasilinearization offers a possible advantage over other methods since only the known boundary conditions and the optimality requirement are satisfied at each iteration. This frees the algorithm from attempting to meet many restrictions at each trial. This freedom could lead to more rapid convergence than that obtained by other techniques.

TABLE 2. INITIAL ADJOINT VARIABLE AS A FUNCTION OF ITERATION NUMBER

Integration step size = 0.1 min. Computation time = 20 sec.

Iteration No.	$z_1(0)$	$z_2(0)$
0	−0.50896	−0.90617
1	−0.59719	−0.89007
2	−0.60606	−0.83272
3	−0.60995	−0.82827
4	−0.61000	−0.82824

TABLE 3. INITIAL ADJOINT VARIABLE AS A FUNCTION OF ITERATION NUMBER

Integration step size = 0.01 min. Computation time = 3 min.

Iteration No.	$z_1(0)$	$z_2(0)$
0	−0.28159	−0.97568
1	−0.73965	−1.40106
2	−0.58817	−0.93602
3	−0.59690	−0.83613
4	−0.60985	−0.82806
5	−0.60999	−0.82825

Note Added In Proof: In a recent presentation, Schley and Lee [*Joint Auto. Control Conf. Preprints*, 186 (1966)] propose a modification of the quasilinearization-invariant imbedding algorithm presented above. They note the equivalence between $\mathbf{R}(t, \mathbf{x}^{(k+1)}(t))$ and $\mathbf{z}^{(k+1)}(t)$. This eliminates the need for generating $\mathbf{z}^{(k+1)}(t)$ by forward integration of the linearized adjoint equation, which is often complicated by numerical instabilities.

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NOTATION

E_1, E_2 = activation energy, cal./mole
f_i = function defined by Equation (1)
g_i = function defined by Equation (9)
G_1, G_2 = pre-exponential factor in Arrhenius expression, min.$^{-1}$
H = Hamiltonian function
I = performance index
k_1, k_2 = reaction rate constants, min.$^{-1}$
M_{ij}, N_i = dependent variables defined by Equation (25)
R = gas constant
R_i = dependent variable defined by Equation (12)
S_{ij}, S_i = constants in Equations (22) and (23)
t = independent variable
t_{ij}, t_i = constants in Equations (22) and (23)
T = temperature, °K.
u_i = control variable
x_i = state variable
z_i = adjoint variable
z_i^j = element of Green's tensor
Δ = differential change in t_o
λ = constant in Equation (32)
σ_{ij}, τ_{ij} = constants in Equations (22) and (23)

Superscripts

f = final
(k) = k^{th} approximation
0 = initial

Subscripts

f = final
0 = initial

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The Gas and Liquid Solubility Relations in Hydrocarbon-Water Systems

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The typical solubility boundaries of binary simple hydrocarbon-water systems are outlined for temperatures and pressures ranging into the neighborhood of the critical point for pure water. These systems are characterized by two unique states, a critical vaporization end point and a critical solution end point. The former defines the limit of mutual solubility of two liquid phases, and the latter defines a point of complete solubility at a minimum pressure. Experimental *P-T-x* data for cyclohexane-water and *n*-hexane–water mixtures are presented.

Traditionally the solubilities of hydrocarbon-water systems are described in terms of specific phase boundaries within the liquid state. In many instances liquids dissolved in liquids are indicated (*1, 2*), while for some lighter hydrocarbons, gases dissolved in liquids may also be reported. Extensions and correlations of these data theoretically (*3* to *5*) or empirically (*6*), either within a particular hydrocarbon-water system or among systems in general, are limited in scope. Some consider only the hydrocarbon-rich phase or the solubility of water in hydrocarbon; others consider only atmospheric pressure solubilities, and nearly all are limited to temperatures below 250°C. However, when the solubility boundaries of these systems over their entire temperature range are viewed, a not altogether unexpected similarity is found.

DESCRIPTION OF THE SOLUBILITY BOUNDARIES

Qualitatively summarized in Figure 1 are the essential solubility boundaries typical of the hydrocarbon-water binary behavior up to the neighborhood of the critical temperature and pressure of pure water. In lighter outline in Figure 1 are two sets of isobaric heterogeneous phase boundaries characteristic of lower and higher pressure behavior.

Familiarly, at a constant lower pressure the solubility of water in hydrocarbon, curve *AB*, and hydrocarbon in water, curve *DE*, increases with increasing temperature when the solubility is limited by the incidence of a second liquid phase. Further increase in temperature at the same lower constant pressure shows that the solubility decreases, curves *BC* and *EF*, when the second impending phase is gaseous.

The maximum solubilities in either liquid phase at a particular lower pressure therefore occur at the temperature of point *B* or *E* when the second phase is the heteroazeotropic vapor of composition *G*. The locus of all points such as *B* and *E* forms the essential boundaries of the saturated solubility diagram. At point *H* the hydrocarbon-rich liquid and the heteroazeotropic vapor compositions become identical. This unique point is called the *critical vaporization end point* (*7*).

At a higher constant pressure the solubility of a hydrocarbon in water, although greater, is affected by increasing temperatures in the same manner as at a lower pressure. Compare curves *DLK* and *DEF*. At this same constant higher pressure the solubility of water in a hydrocarbon, although nominal at lower temperatures, increases infinitely with increasing temperature as depicted by curve *AJK*. The point *J* is located on this curve at the temperature corresponding to point *L* (the saturated solubility of hydrocarbon in water) and has no other real significance. The curve segment *JK* does appear however as the water solubility in gaseous hydrocarbons, which is more commonly referred to as a *dew-point locus*. The remainder of the curve from *J* to *A* must then be identified as a liquid-

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