

mining the upper limit of the applicability of this correlation; however, it is thought that it will apply at all vapor velocities where the tray is operating in the froth regime from below the point at which the tray commences weeping, up to the point of transition from the froth to spray regimes.

At hole load factors greater than 0.9 m/s,  $Z$  is between 0.9 and 1.0, and so in this range the correction to the dry tray correlation is of only small significance. However, below 0.9 m/s the correction becomes more important, particularly as this is the more likely operating range for modern large hole trays with high free areas.

## CONCLUSIONS

Use of a correction to the dry tray orifice equation provides a useful design correlation for pressure drop in terms of the liquid head on the tray, superficial vapor velocity, system properties, and tray geometry. This correction is most significant at values of hole load factor below 0.9 m/s.

## NOTATION

$Co$	= dry tray orifice coefficient
$Cw$	= wet tray orifice coefficient
$F$	= tray free area (that is, fraction of the perforated tray area occupied by holes)
$g$	= gravitational acceleration, cm/s
$h_L$	= static liquid head, cm
$h_R$	= residual head, cm
$h_v$	= head loss by vapor passing through the liquid, cm
$h_{DT}$	= head loss across dry tray, cm
$h_{WT}$	= head loss across tray with froth present, cm

$P$	= pressure drop across operating tray, cm
$V_s$	= superficial vapor velocity, cm/s
$V_H$	= vapor velocity through perforations, cm/s
$Y$	= expansion factor
$Z$	= bubbling factor
$\rho_L$	= liquid density
$\rho_v$	= vapor density

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# An Approach to Mechanism Discrimination in Free-Radical Reactions

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There has been considerable interest over the past 10 yr. in the treatment of kinetic mechanisms involving active intermediates which may be experimentally unobservable for all or part of the reaction time. Examples of such reaction systems include free radicals in homogeneous pyrolysis and oxidation reactions, active surface compounds in catalytic systems, and enzymes in biochemical systems.

By their nature, such sets of reactions involving active intermediates have two different time scales, and the dynamic behavior of such systems leads invariably to a stiff set of differential equations with widely differing eigenvalues. A significant amount of attention has been focused on methods of solving such equations numerically (Seinfeld et al., 1970; Gear, 1971; Sena and Kershenbaum, 1975; Denis and Daubert, 1974), and several generally successful algorithms are available.

However, in the absence of any good estimates of the rate constants involved or even of the viability of a proposed reaction mechanism, it is often more important to test some preliminary experimental data on such systems to see if they are consistent with the proposed mechanism.

A usual procedure in this direction is to invoke the well-known quasi steady state approximation (QSSA). This reduces some of the differential equations to algebraic ones and often allows the remaining differential equations to be solved analytically. Bowen et al. (1963) showed that, in fact, the QSSA was generally the first term in a singular perturbation solution of the complete problem, and Aiken and Lapidus (1974) have recently devised an effective numerical integration method based on that principle.

In this work, a systematic approach has been outlined for the study of systems of chemical reactions involving active intermediates. By utilizing existing theory with some small extensions, it has been possible to show that such systems have built into them a set of constraints which must be satisfied by any proposed mechanism seeking to explain the kinetics of the system.

## THEORY

The singular perturbation approach to the solution of problems in kinetics seeks to put the differential equations describing the system in the form

$$\frac{dx}{dt} = f(t, x, y, \epsilon) \quad \epsilon \frac{dy}{dt} = g(t, x, y, \epsilon) \quad (1)$$

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where  $\epsilon$  is generally a small parameter. One then seeks a solution of the form

$$\begin{aligned} \mathbf{x} &= \mathbf{x}_0(t) + \mathbf{x}_1(t) \phi_1(\epsilon) + \mathbf{x}_2(t) \phi_2(\epsilon) + \dots \\ \mathbf{y} &= \mathbf{y}_0(t) + \mathbf{y}_1(t) \phi_1(\epsilon) + \mathbf{y}_2(t) \phi_2(\epsilon) + \dots \end{aligned} \quad (2)$$

where the  $\phi_i(\epsilon)$  are generally simple functions of  $\epsilon$  (often powers of  $\epsilon$ ).

The degenerate solution (or quasi steady state solution)  $\mathbf{x} = \mathbf{x}_0$ ,  $\mathbf{y} = \mathbf{y}_0$  obtained by setting  $\epsilon = 0$  in Equations (1) will clearly not generally satisfy the initial conditions on  $\mathbf{y}$  and hence will not be valid as  $t \rightarrow 0$ .

For small values of  $t$ , a different series expansion (the inner or boundary-layer solution) is required. The details of these solutions together with the necessary initial conditions for (1) are described by Bowen (1963), Vasil'eva (1963), O'Malley (1968), and others.

Before we attempt to solve problems of this type, it would be extremely helpful to reject obviously erroneous proposals, or, alternatively, to have some a priori information about the relative values of some of the rate constants, consistent with the proposed mechanism. Let us consider, then, the case of a complex set of chemical reactions involving some type of short-lived active intermediate occurring isothermally in a closed system. The entire set of reactions leads to a system of ordinary differential equations

$$\frac{d\mathbf{c}}{dt} = \boldsymbol{\beta}^T \mathbf{r}(\mathbf{c}, k) \quad \mathbf{c}(0) \text{ given} \quad (3)$$

The space spanned by all the reactions is the stoichiometric space  $S$ . In order to formulate the dynamic behavior of the system as a singular perturbation problem, we must consider the conditions under which the space  $S$  can be decomposed into two subspaces  $S_1$  and  $S_2$  such that, for some period of time, the projection of the trajectory of the system on  $S_1$  is large compared with the projection on  $S_2$ . In chemical kinetics the situation is often encountered in which the decomposition of  $S$  corresponds simply to a natural partition of the chemical species into  $\mathbf{c}_1$  and  $\mathbf{c}_2$ , where  $\mathbf{c}_1$  represents the vector of stable species and  $\mathbf{c}_2$  represents the vector of active intermediates. Let us investigate the constraints arising out of such a partition, extending some earlier work by Horiuti and Nakamura (1957).

#### Stoichiometric Constraints

Consider the case of active intermediates in which Equation (3) can be partitioned into

$$\frac{d}{dt} \begin{bmatrix} \mathbf{c}_1 \\ \mathbf{c}_2 \end{bmatrix} = \begin{bmatrix} \boldsymbol{\beta}_1^T \\ \boldsymbol{\beta}_2^T \end{bmatrix} \mathbf{r} \quad (4)$$

If a degenerate system exists, it will be characterized by

$$\mathbf{0} = \boldsymbol{\beta}_2^T \mathbf{r} \quad (5)$$

That is,  $\mathbf{r}$  is an element of the kernel (null space) of  $\boldsymbol{\beta}_2^T$ . Let this space,  $\ker \boldsymbol{\beta}_2^T$  have as a basis a set of vectors  $\mathbf{N} = \mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_p$ , where the vectors  $\mathbf{v}_i$  are solutions of

$$\boldsymbol{\beta}_2^T \mathbf{v} = \mathbf{0} \quad (6)$$

Each independent vector  $\mathbf{v}$  can be thought of as a reaction path leading to an overall stoichiometry (involving no active intermediates) described by the transformed stoichiometric matrix  $\boldsymbol{\beta}^{*T}$ , where

$$\boldsymbol{\beta}^{*T} = \boldsymbol{\beta}_1^T \mathbf{N} \quad (7)$$

(Some linear combinations of  $\mathbf{v}$ , however, can lead to a blank route where the overall stoichiometry is null,  $\mathbf{0} \rightarrow \mathbf{0}$ ).

Finally, since  $\mathbf{N}$  is a basis for  $\ker(\boldsymbol{\beta}_2^T)$ , and by Equations

(5)  $\mathbf{r}$  is an element of  $\ker(\boldsymbol{\beta}_2^T)$ , we can define a transformed rate of reaction vector  $\mathbf{r}^*$  where

$$\mathbf{r} = \mathbf{N} \mathbf{r}^* \quad (8)$$

and  $\mathbf{r}^*$  is a vector whose components are the rates of reaction along each of the conceptual reaction paths given by (7).

Many complex reactions, when subjected to the above analysis, indicate that there can be several reaction paths, via different combinations of active intermediates, leading to the same overall stoichiometry. If the original mechanistic hypothesis regarding partitioning is to be valid, then the system must obey the predicted overall stoichiometry. If, on the basis of preliminary experimental data, the predicted overall stoichiometry is not obeyed, then the proposed mechanism may be rejected.

In other reaction systems, the various reaction paths can lead to different overall stoichiometries. One can follow Temkin's approach (1963) and define a global stoichiometry representing the relative contribution of each overall route.

The global contribution of each reaction is given by

$$\mathbf{v}^{\Sigma} = \frac{r_1^*}{\Sigma r_i^*} \mathbf{v}_1 + \dots + \frac{r_p^*}{\Sigma r_i^*} \mathbf{v}_p$$

The global stoichiometry is given by  $\boldsymbol{\beta}^{\Sigma T} = \boldsymbol{\beta}_1^T \mathbf{v}^{\Sigma}$ , and the system moves along this stoichiometry with an overall rate  $r^{\Sigma} = \Sigma r_i^*$ . Here again, a constraint is placed on the global stoichiometry of the system, as will be illustrated in the second example below. In either case, some simple algebraic manipulation of the stoichiometry leads to a consistency test for a proposed mechanism.

#### Dynamic Constraints

If such a partition is to be kinetically (as well as stoichiometrically) feasible, then some relationship between the rate constants must exist such that, in fact, the projection of the trajectory on  $S_2$  is indeed much smaller than its projection on  $S_1$ . If the conditions are not met in a given situation, then a solution of the derived form will not be possible.

The dynamic constraints can be expressed as a further restriction on the stoichiometric constraints. By using the above approach, equations can be obtained for the degenerate concentrations  $\mathbf{c}_1^*$  and  $\mathbf{c}_2^*$ . Then, in order for the solution to be valid, the dynamic constraint can be expressed as

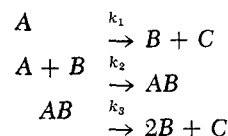
$$\left\| \frac{d\mathbf{c}_2^*}{dt} \right\| \approx \epsilon \left\| \frac{d\mathbf{c}_1^*}{dt} \right\| \quad (9)$$

where  $\epsilon$  is a small parameter. In general, the smallness of this parameter implies corresponding restrictions on some values of the ratios of rate constants or some other limitations.

#### EXAMPLES

##### Autocatalysis

One of the most interesting mechanisms which has been investigated by singular perturbation techniques has been the Waller and Platt (1967) mechanism for autocatalysis as discussed by Schneider, Amundson, and Aris (1972). The elementary reactions are



where  $\text{AB}$  is some intermediate complex.

Let us look at the same mechanism first from the point of view of stoichiometric constraints and then of kinetic constraints.

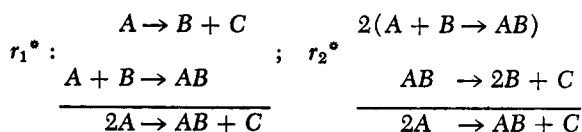
For  $c = ([A] [B] [C] [AB])^T$ ,

$$\beta^T = \begin{bmatrix} -1 & -1 & 0 \\ 1 & -1 & 2 \\ 1 & 0 & 1 \\ 0 & 1 & -1 \end{bmatrix}$$

and one can proceed to test the possibilities, in turn, that  $B$ ,  $AB$ ,  $A$ ,  $C$  are active intermediates for some period of the reaction. If  $B$  is the active intermediate, as proposed by Schneider et al.,  $\beta_2^T = [1 \ -1 \ 2]$ , and solving Equation (6) we get  $v_1 = [1 \ 1 \ 0]^T$  and  $v_2 = [0 \ 2 \ 1]^T$ . The overall stoichiometric matrix  $\beta^{*T}$  is given by Equation (7),

$$\beta^{*T} = \beta_1^T N = \begin{bmatrix} -2 & -2 \\ 1 & 1 \\ 1 & 1 \end{bmatrix}$$

yielding an overall stoichiometry  $2A \rightarrow AB + C$ . Here, one can consider the overall stoichiometry to consist of two two-step reactions, and their rates of reaction are  $r_1^*$  and  $r_2^*$ :



Applying Equation (8), we get

$$\begin{aligned} r_1 &= r_1^* = k_1 [A]^* \\ r_2 &= r_1^* + 2r_2^* = k_2 [A]^* [B]^* \\ r_3 &= r_2^* = k_3 [AB]^* \end{aligned}$$

and the degenerate concentration of the active intermediate  $[B]^*$  is given by

$$[B]^* = \frac{k_1}{k_2} + \frac{2k_3}{k_2} \frac{[AB]^*}{[A]^*} \quad (10)$$

For the dynamic constraints,  $\frac{d[B]^*}{d[A]^*}$  can be computed from (10) to give

$$\frac{d[B]^*/dt}{d[A]^*/dt} = \frac{d[B]^*}{d[A]^*} = \frac{-k_3}{k_2[A]_0} \frac{2 - \eta}{(1 - \eta)^2} \quad (11)$$

where  $\eta$  is the extent of the overall reaction and is equal to  $(1 - [A]^*/[A]_0)$ . In this case, if the criterion (9) is to be met, two constraints must be satisfied:

$$\frac{k_3}{k_2[A]_0} \approx \epsilon, \text{ a small parameter, and } \eta \ll 1$$

The above case is, in fact, the one investigated by Schneider et al., who found, not surprisingly, that the singular perturbation solution changed drastically when the second condition was no longer satisfied. When the conversion approaches 1, the behavior of the system tends towards the case where  $A$  (the main reactant) is in a stationary state. Application of the above analysis to such a situation shows that the overall stoichiometry when  $\eta \rightarrow 1$  becomes  $AB \rightarrow 2B + C$ .

An alternative approach is to consider the possibility that  $AB$  is the active intermediate. Under these conditions,  $\beta_2^T = [0 \ 1 \ -1]$  and solving Equation (6) yields  $v_1 = [1 \ 0 \ 0]^T$ ;  $v_2 = [0 \ 1 \ 1]^T$ , which gives an overall stoichiometry  $A \rightarrow B + C$ . Similarly, for the dynamic constraints, one can compute

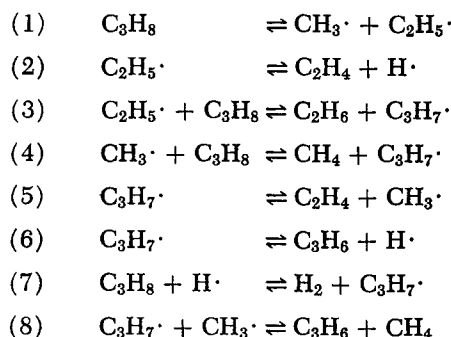
$$\frac{d[AB]^*}{d[A]^*} = \frac{k_2[A]_0}{k_3} (2\eta - 1) \quad (12)$$

where  $\eta$  is the extent of the overall reaction. Clearly, the criterion (9) will only be met if  $\frac{k_2[A]_0}{k_3} \sim \delta$ , a small parameter, the inverse of the constraint obtained when  $B$  is the active intermediate. It can be shown (by singular perturbation solution or otherwise) that this mechanism also exhibits autocatalytic behavior.

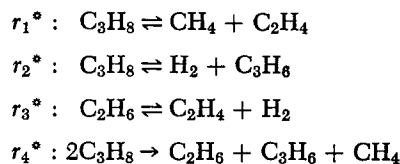
However, although we have two conflicting mechanisms which predict autocatalysis, the analysis has placed stoichiometric constraints and kinetic constraints on the two possible mechanisms, both of which are mutually exclusive. Experimental discrimination between the two should not be difficult.

#### Propane Pyrolysis

A second example, illustrating another type of stoichiometric constraint, is the case of hydrocarbon pyrolysis, following a mechanism proposed by Herriott et al. (1972). The pyrolysis of propane is to consist of the following elementary steps:



Taking the radicals as the active intermediates and going through a similar analysis, we get to the following stoichiometries:



or any linear combination thereof.

Note that in this case each of the overall reaction paths has a different stoichiometry. The first three correspond to various sets of propagation reactions, while the last one represents the initiation and termination steps. The global rate of reaction  $r^\Sigma = r_1^* + r_2^* + r_3^* + r_4^*$ , and the global stoichiometry is given by

$$\beta^\Sigma = \beta_1^T v^\Sigma = \frac{1}{r^\Sigma} \begin{bmatrix} r_2^* + r_3^* \\ r_1^* + r_4^* \\ r_4^* - r_3^* \\ r_1^* + r_3^* \\ -r_1^* - r_2^* - 2r_4^* \\ r_2^* + r_4^* \end{bmatrix} \quad (13)$$

for  $c_1 = ([H_2] [CH_4] [C_2H_6] [C_2H_4] [C_3H_8] [C_3H_6])^T$ .

Again, there are stoichiometric constraints placed on this complex system. For example, Equation (13) dictates the stoichiometric constraint that  $[CH_4] \simeq [C_2H_6] + [C_2H_4]$ . If this is not borne out by experimental data, then the proposed mechanism can not be correct for these active intermediates.

In fact, examination of the data by Herriott et al. (1972) shows a reasonable agreement with the stoichio-

metric constraints of Equation (13), and the proposed mechanism can not be ruled out.

## CONCLUSIONS

It has been shown that reaction systems with active intermediates are amenable to a straightforward analysis of the constraints imposed by stoichiometry and kinetics. These constraints yield considerable information about the structure of the general solution. Examples have been given of the application of the analysis to systems of varying complexity.

## ACKNOWLEDGMENT

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## NOTATION

- $c$  = vector of concentrations  
 $c_1, c_2$  = vectors of concentrations of stable and active species, respectively  
 $k$  = vector of rate constants  
 $N$  = basis for null space of  $\beta_2^T$   
 $r$  = vector of rates of reaction  
 $t$  = time  
 $x, y$  = state variables

## Greek Letters

- $\beta$  = stoichiometric matrix  
 $\beta_1, \beta_2$  = partitioned stoichiometric matrix  
 $\delta, \epsilon$  = small parameters  
 $\eta$  = dimensionless extent of reaction  
 $v$  = vectors in null space of  $\beta_2^T$

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# A Method of Temperature Estimation in the Bubble Point Method of Iterative Distillation Calculations

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A general procedure for distillation calculation has been discussed by several authors, for example, Amundson et al. (1959), Holland (1963), Wang and Henke (1966), and Billingsley (1970). The procedure is summarized as follows: (1). assume an initial phase flow and temperature profiles; (2). calculate the vapor-liquid equilibrium constant of each component at each stage  $K_{ij}$ ; (3). solve the material balance equations for the composition of each component at each stage. (4). The stage temperature is determined in a manner explained subsequently; (5). the phase flow rates are computed by the energy balance; and (6). steps (2) through (5) are repeated in order until  $|(T_j)_n - (T_j)_{n-1}| < E_T$  for each stage where  $E_T$  is a pre-described tolerance.

Billingsley (1970) pointed out that the stage temperature determination is the least satisfactory part of any published scheme solving distillation problems. In the conventional bubble point method of iterative distillation calculation, the temperature profile in the column is estimated

on the basis of the liquid composition at each stage by bubble point temperature calculation or the vapor composition by dew point temperature calculation. Wang and Henke (1966) used Muller's method to obtain the bubble point or dew point temperature, while most of the other investigators used the Newton-Raphson iterative method. Holland (1963) suggested that temperature for each stage can be approximated by the  $K_b$  method. Billingsley (1970) proposed an improvement in the  $K_b$  method.

The objective of this article is to present a new method, called the *hypothetical component method*, which provides a simple way to estimate the bubble point or dew point temperature for each stage.

## HYPOTHETICAL COMPONENT METHOD

For convenience, we will delete the stage index; however, the reader should keep in mind that the derivation given is applicable to each stage. Let us assume that the