Synthesis of Kinetic Structure of Reaction Mixtures of Irreversible First-Order Reaction

A synthesis method for the kinetically consistent structure of reaction mixtures is developed based on elementary structures of reaction mixtures and rate expressions for product lumps of n^{th} order. Knowledge of product lumps and experimental kinetic data on each of the lumps are required for the synthesis of kinetic structure. Rate constants for all reaction paths and initial lumps from which all the product lumps originate can be determined.

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SCOPE

Reaction mixtures usually result from reactions involving natural material such as petroleum, coal, wood, and biological material. These reaction mixtures are typified by many species participating in the overall reaction. Reaction products of interest are sums of some of the species lumped together (lumps). Lumping of species for the product lumps is usually a necessity. Reaction mixtures are usually characterized by lack of knowledge of the origin of product lumps (initial lumps) and pseudo first- or first-order reaction that each reaction path follows. Typical examples are catalytic cracking of gas oil and thermal decomposition of coal.

Aris and Gavalas (1966) were among the first to study reaction mixtures. The concept of using initial rate constant distribution (Aris, 1968) was used by Luss and co-workers (1971, 1974, 1975) in arriving at useful results. Pitfalls in using empirical lumping kinetics were pointed out by them. Weekman and co-workers (for instance, 1971, 1976) did extensive studies on catalytic cracking of gas oil. Wei and Kuo (1969) and Ozawa (1973) developed lumping requirements.

An important problem in studying reaction mixtures is that of synthesizing a kinetic structure for all the lumps in the mixture in such a way that the observed kinetic behavior of product lumps can be explained. It is the main objective of this paper to develop rules for the synthesis of a kinetically consistent structure for reaction mixtures of irreversible first-order reaction. Elementary structures of reaction mixtures are analyzed to arrive at some of the synthesis rules. A rate expression developed by Lee (1977) for reaction mixtures with many first-order reactions is utilized for additional synthesis rules. These synthesis rules are then applied to a reaction mixture of eight product lumps and unknown number of initial lumps to synthesize a kinetically consistent structure of the reaction mixture.

CONCLUSIONS AND SIGNIFICANCE

A set of rules is presented for synthesizing a kinetically consistent structure of reaction mixtures of irreversible first-order reaction. These rules are derived from elementary structures of reaction mixtures such as integral, differential, and formation/disappearance structure and from a rate expression of an n^{th}-order linear differential equation for product lumps. Given product lumps and kinetic data on each of the lumps, kinetic structure of a reaction mixture can be synthesized by using the rules as illustrated by an example. Knowledge of initial lumps is not necessary. A skeleton structure is first established for synthesis, which is characterized by distinct rate constants. Kinetic behavior of any lump in a reaction mixture can be described by linear combinations of exponentials of these rate constants.

Application of the rules to real processes would not be straightforward but would require trial and error and engineering judgments. Real value of the synthesis method obtained is in reducing tremendous number of possible kinetic structures down to several structures that can be further tested. The method also produces candidates for kinetically consistent initial lumps which are usually difficult to identify. A by-product of the synthesis is rate constants determined for all reaction paths of a reaction mixture.

Some theoretical as well as practical advances have been made in dealing with reaction mixtures where many species participate in the overall reaction and yet the products of interest are sums of species lumped together. Aris and Gavalas (1966) were among the first to study continuous reaction mixtures. They arrived at some specific results by assuming the functional form of rate kernels. Aris (1968) introduced the concept of using assumed initial distribution of rate constants. This concept was used in various forms by several workers. Luss and Hutchinson (1971) and Golikeri and Luss (1974, 1975) obtained useful results for the grouping of many species and pointed out pitfalls in using some of the empirical lumping kinetics. One of their findings was that traditional kinetic approach is not adequate for the reaction mixtures. Wei and Kuo (1969) and Ozawa (1973) obtained lumpability and lumping requirements of species in reaction mixtures for which reaction paths and rate constants are known. On the practical side, Nace et al. (1971) and Jacob et al. (1976) studied catalytic cracking of gas oil. Anthony and Howard (1976) used an assumed distribution of activation energy for coal devolatilization.

Although some useful results have been obtained for

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the reaction mixtures based on accumulation of knowledge on the practical side and based on a few approaches on the theoretical side, there are still various aspects of reaction mixtures that require further studies. In this paper, synthesis of reaction paths of reaction mixtures is investigated based on the kinetic expression of an n^{th}-order linear differential equation for reaction mixtures (Lee, 1977).

Reaction mixtures in general result from the reactions of natural material. Of importance are reactions involving petroleum, coal, wood, and biological material. These reaction mixtures are characterized by:

1. Reaction products of interest are sums of species lumped together. Individual species in the lump does not necessarily originate from the same reactant (origin).
2. These lumped products are normally measurable directly or inferrable from other indirect measurements.
3. Precise origin of lumped products is not necessarily known. For instance, it is not precisely known what components of coal eventually end up in secondary gases produced by coal devolatilization. It will be assumed that each reaction path follows irreversible first- or pseudo first-order reaction. Typical examples are catalytic cracking of gas oil, thermal decomposition of coal, pulping of wood, and biological oxygen demand.

The characteristics of reaction mixtures described above will be used as given conditions for further development.

At the core of the problems in dealing with reaction mixtures is finding reaction paths connecting all the product lumps and initial lumps in such a manner that the observed kinetic behavior of product lumps can be explained, given only the lumped products of interest with no a priori knowledge on the reaction paths or rate constants. Even when considerable amount of knowledge has been accumulated for a reaction mixture, synthesizing a kinetically consistent structure for reaction mixtures is by no means a trivial matter as indicated, for instance, by Jacob et al. (1976) in their study for catalytic cracking of gas oil.

Species in the raw reactant lumped together is to be called initial lump. All of the product lumps originate from the initial lumps (I_1 and I_2 lump in Figure 1). Proper selection of initial lumps is critical for any kinetic study of reaction mixtures, since improper selection would make rate constants vary with composition of raw reactant. The total sum of initial lumps is to be called raw

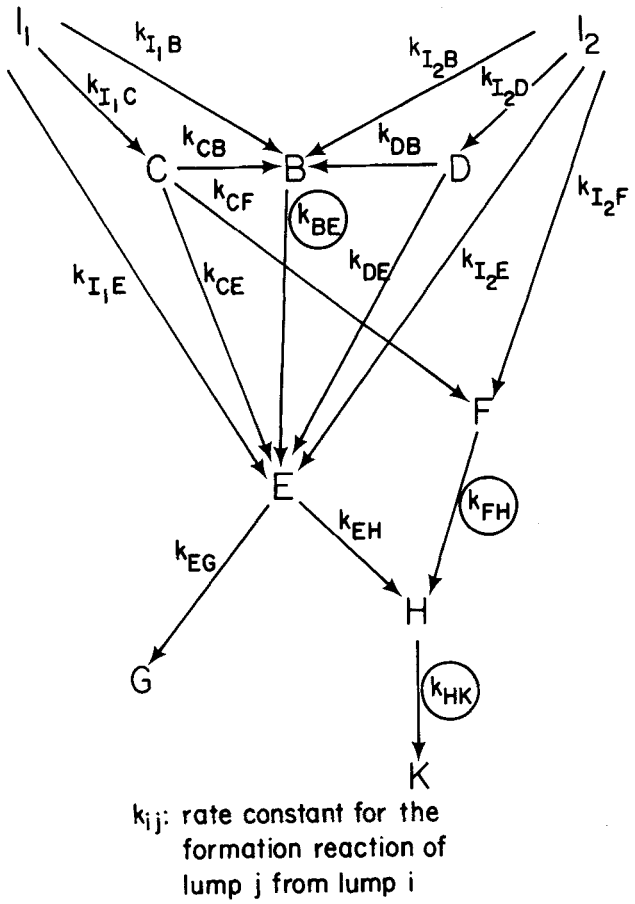


Fig. 1. Kinetic structure of a reaction mixture.

reactant. Typical examples are particular grade of oil and coal. A product lump which does not have any disappearance reaction path is to be called terminating lump (G and K in Figure 1). Product lumps are the lumps normally identified as products of a reactor or a process.

Synthesis and Elementary Structures of Reaction Mixtures

It was shown that kinetic behavior of a reaction mixture with many first-order reactions could be represented

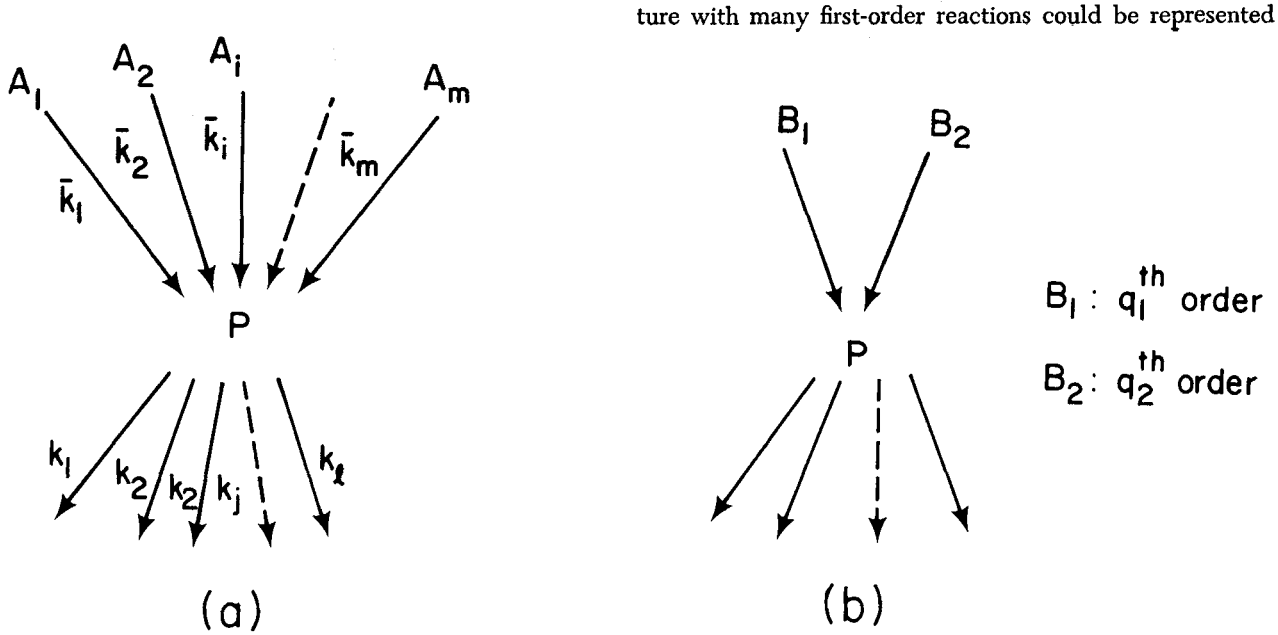


Fig. 2. Formation/disappearance structure.

TABLE 1

Given lumps	B	C	D	E	F	G	H	K
n	5	2	2	6	4	6	8	8
Q	0	0	0	0	0	Nonzero	0	Nonzero

TABLE 2

Lump	Distinct rate constants [Eigenvalues of Equation (1)]
C	K_{I_1}, K_C
D	K_{I_2}, K_D
B	$K_{I_1}, K_{I_2}, K_C, K_D, k_{BE}$
E	$K_{I_1}, K_{I_2}, K_C, K_D, k_{BE}, K_E$
F	$K_{I_1}, K_C, K_{I_2}, k_{FH}$
G	$K_{I_1}, K_{I_2}, K_C, K_D, k_{BE}, K_E$
H	$K_{I_1}, K_{I_2}, K_C, K_D, k_{BE}, K_E, k_{FH}, k_{HK}$
K	$K_{I_1}, K_{I_2}, K_C, K_D, k_{BE}, K_E, k_{FH}, k_{HK}$

Eight distinct eigenvalues:

$$K_{I_1}, K_{I_2}, K_C, K_D, k_{BE}, k_{FH}, k_{HK}, K_E$$

$$K_{I_1} = k_{I_1B} + k_{I_1C} + k_{I_1E}$$

$$K_C = k_{CB} + k_{CF} + k_{CE}$$

$$K_{I_2} = k_{I_2B} + k_{I_2D} + k_{I_2E} + k_{I_2F}$$

$$K_D = k_{DB} + k_{DE}$$

$$K_E = k_{EG} + k_{EH}$$

by an n^{th}-order linear differential equation if there were only one product lump containing all the species in the mixture (Lee, 1977). Applying the results for any j^{th} product lump, we have

$$L^{n_j}(x_j) = Q_j \quad j = 1, \ldots p \tag{1}$$

where

$$L^{n_j} \equiv (D^{n_j} + a_{1_j}D^{n_j-1} + \ldots + a_{n-1_j-1}D + a_{n_j})$$

$$D \equiv d/dt$$

and a_{n_j}'s are a function of rate constants only. A lump represented by an n^{th}-order linear differential equation is to be called n^{th}-order lump. An n^{th}-order lump has n distinct exponential terms and at most n kinetically distinct reaction paths. Otherwise, the order cannot be n.

1. Formation and Disappearance Reaction Paths for a Lump

Consider a product lump P in Figure 2*a* with m reaction paths for the formation of P and l reaction paths for the disappearance. We have

$$\frac{dP}{dt} = \sum_{i=1}^{m} W_{A_iP}\bar{k}_iA_i - P\sum_{j=1}^{l} k_j$$

$$= \sum_{i=1}^{m} W_{A_iP}\bar{k}_iA_i - PK, \quad K = \sum_{j=1}^{l} k_j \tag{2}$$

where W_{A_iP} is a stoichiometric coefficient defined by

$$W_{A_iP} = \frac{\text{molecular weight of } A_i}{\text{molecular weight of } P}$$

If A_i were initial lumps, the concentration of lump P would be represented by $(m + 1)$ exponential terms, m from the formation reaction paths and one from the overall disappearance reaction of P, no matter how many disappearance reaction paths there may be. The lump P in that case is $(m + 1)^{th}$ order lump. If A_i were not initial lumps, the order of lumps A_i would determine the order of lump P. This is illustrated in Figure 2*b*. If lumps B_1 and B_2 are q_1^{th} and q_2^{th} order, respectively,

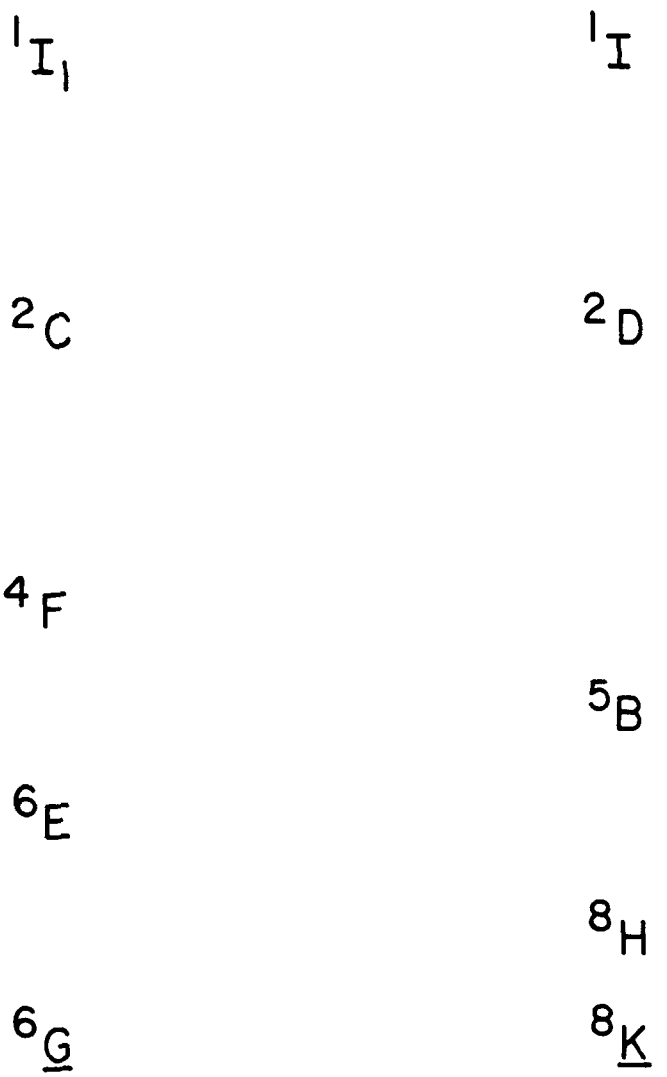


Fig. 3(a).

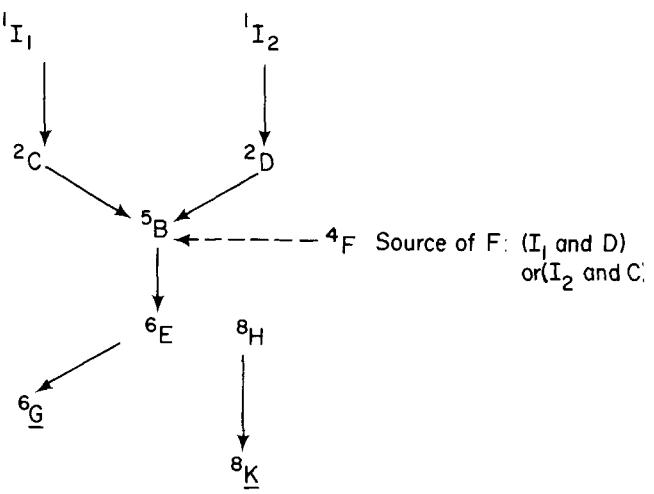


Fig. 3(b).

then the order of lump P is $(q_1 + q_2 + 1)$, provided that lump B_1 is independent of lump B_2. A lump is independent of other lumps if eigenvalues of the characteristic equation of Equation (1) (henceforth to be called eigenvalues or distinct rate constants) for a lump are distinct from those for other lumps. If lumps B_1 and B_2 are not independent of each other, the order of lump P is $(q + 1)$,

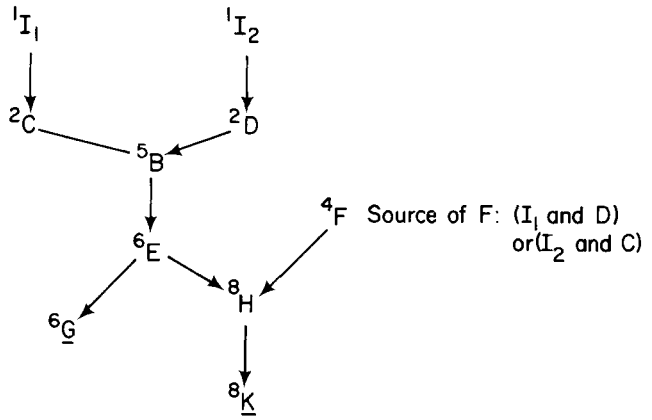


Fig. 3(c). Skeleton structure.

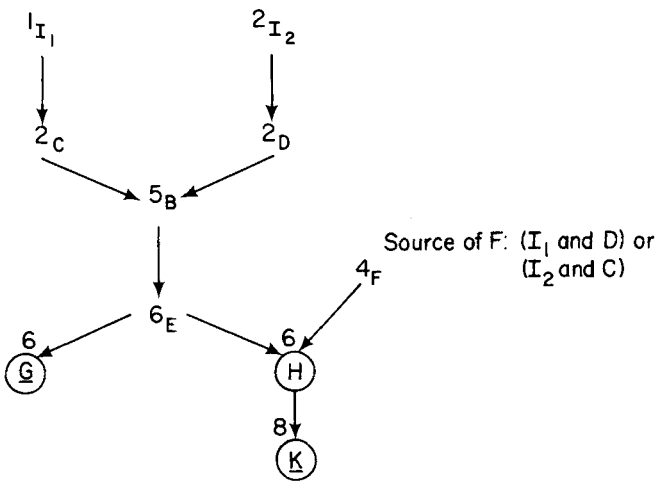


Fig. 3(d).

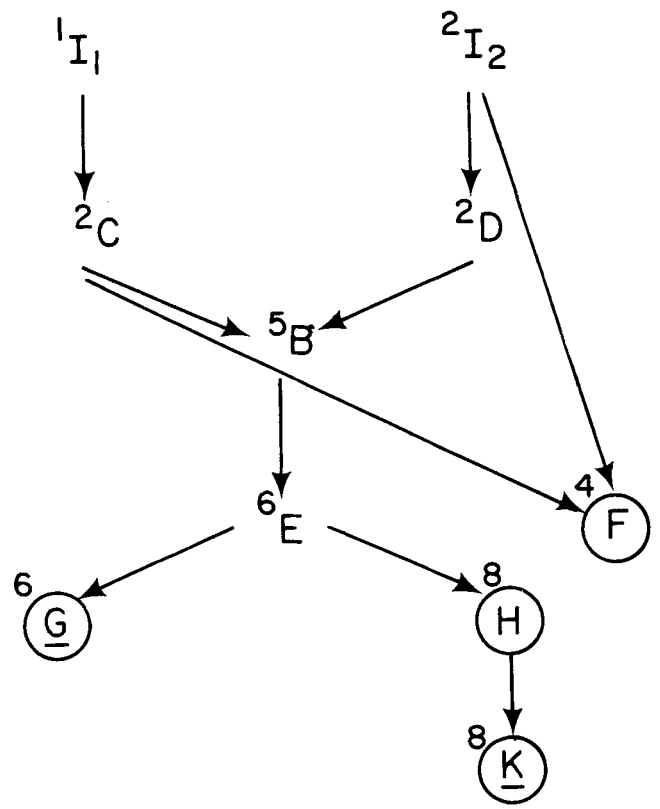


Fig. 3(e).

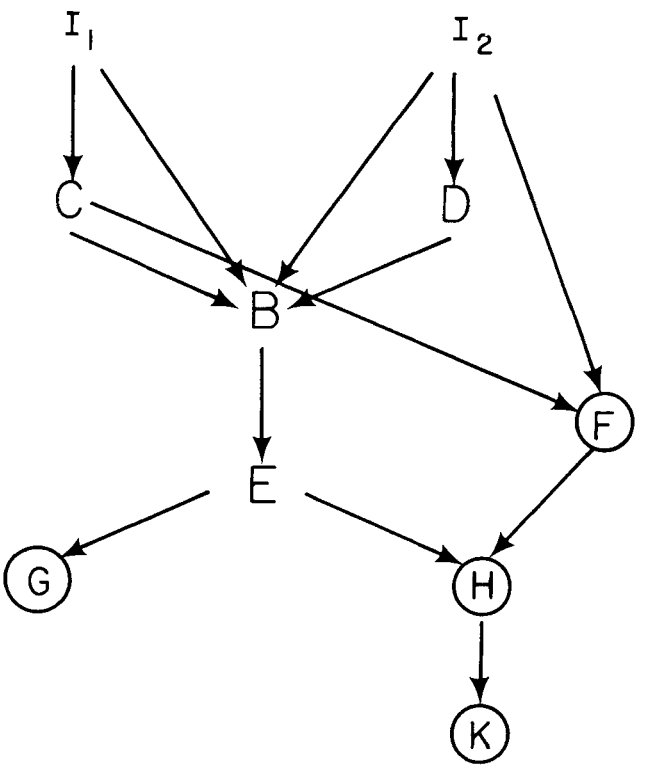


Fig. 3(f).

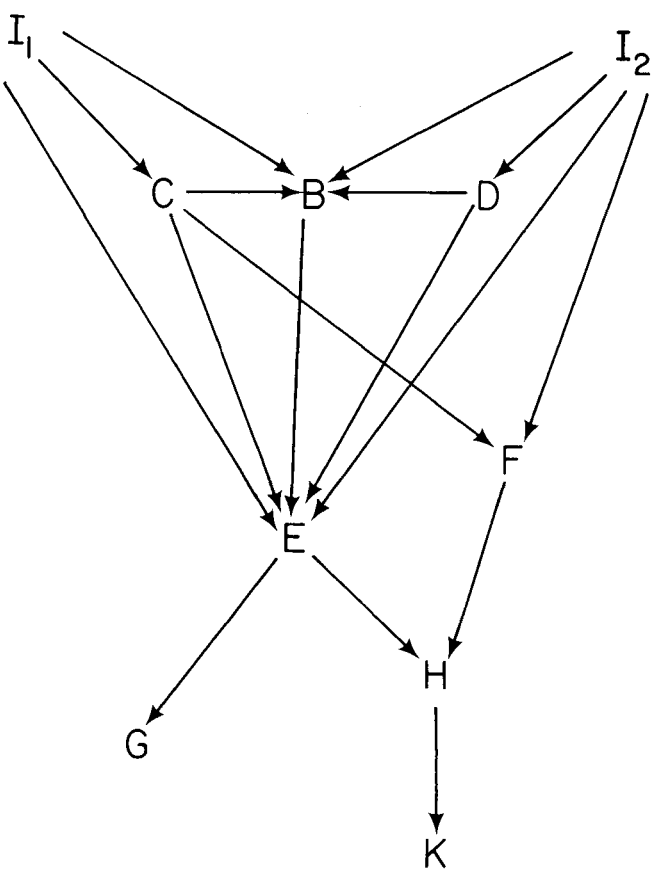


Fig. 3(g).

where q is the number of distinct eigenvalues taken from the pool of q_1 eigenvalues of lump B_1 and q_2 of lump B_2. In such a case, the order q has to be higher than q_1 and q_2 for lumps B_1 and B_2 to be possible source of formation for lump P. Otherwise, lumps B_1 and B_2 cannot be the source of formation for lump P. We state the following rule:

1. In order for a lump M to be a possible source for the formation of another lump N, the order of lump M should be less than that of lump N.

For instance, if lump M is a third-order lump and lump N a fourth-order lump, lump M can be a possible source for the formation reaction of lump N, and there can exist a reaction path from lump M to lump N. If the order of lump M were greater than four and lump M were the source for the formation of lump N, the order of lump N could not be four since the definition of an n^{th}-order lump dictates that the order of lump N be greater than four.

2. *Skeleton Structure*

Skeleton structure is defined as the structure with minimum number of formation paths which are necessary to satisfy the order of each of all the product lumps. The skeleton structure will be used as the basis for synthesizing a kinetically consistent structure of reaction mixtures. A kinetic structure is kinetically consistent if a kinetic structure of a reaction mixture can describe kinetic behavior of all the product lumps in the mixture.

To synthesize a skeleton structure, Equation (1) is used along with formation/disappearance structure. Of particular interest in Equation (1) for the purpose of synthesis are values of Q and n. In the case of terminating lumps for which there is no disappearance reaction, it can be shown that the value of Q for these lumps is nonzero (refer to Appendix A). We note that each of reaction paths follows irreversible first-order reaction.

Given p product lumps and kinetic data on each of the product lumps, we determine n and Q using Lee's method (1977). In general, initial lumps are not known. Of particular interest of all the product lumps are lumps of order of two. Since there has to be disappearance reaction paths for any product lump except for terminating lumps, the product lumps of the order of two must have only one independent formation reaction. Furthermore, it must be formed from one initial lump. Otherwise, the lump cannot be second order. Terminating lumps would be exceptions. We now state the following rules:

2. Any product lump for which Q is nonzero is a terminating lump and is at the bottom of kinetic structure in the sense that there is no disappearance reaction for that lump.

3. Any lump for which $n = 2$ and $Q = 0$ is a product lump formed directly from one initial lump. Initial lumps are first-order lumps.

4. Any product lump of order of n with $Q = 0$ has at least one disappearance reaction path and at most $(n - 1)$ formation paths whose number is independent of the number of disappearance reaction paths of that lump. The number of formation paths could be $(n - 1)$ independent paths or sum of the formation paths from a few or several lumps whose order is less than n. The sum of the number of distinct eigenvalues of those lumps should not be greater than $(n - 1)$ for those lumps to be connected to the n^{th}-order lump.

5. If two lumps are of the same order and one of them is a terminating lump, there exists one formation path for the terminating lump from the other lump.

Suppose a reaction mixture is represented by the kinetic structure in Figure 1. Theoretically, we would have values of n and Q for each lump as given in Table 1. Distinct rate constants (eigenvalues) for each of the lumps are given in Table 2. We will attempt to synthesize the kinetic structure in Figure 1 as we develop synthesis rules and methods.

To form a skeleton structure, we first list the lumps in the order of increasing n as shown in Figure 3*a*. The left uppermost number represents the order of a lump. We list lump G at the bottom, even though n for lump G is less than eight since it is a terminating lump (rule 2). Terminating lumps identified by the value of Q are

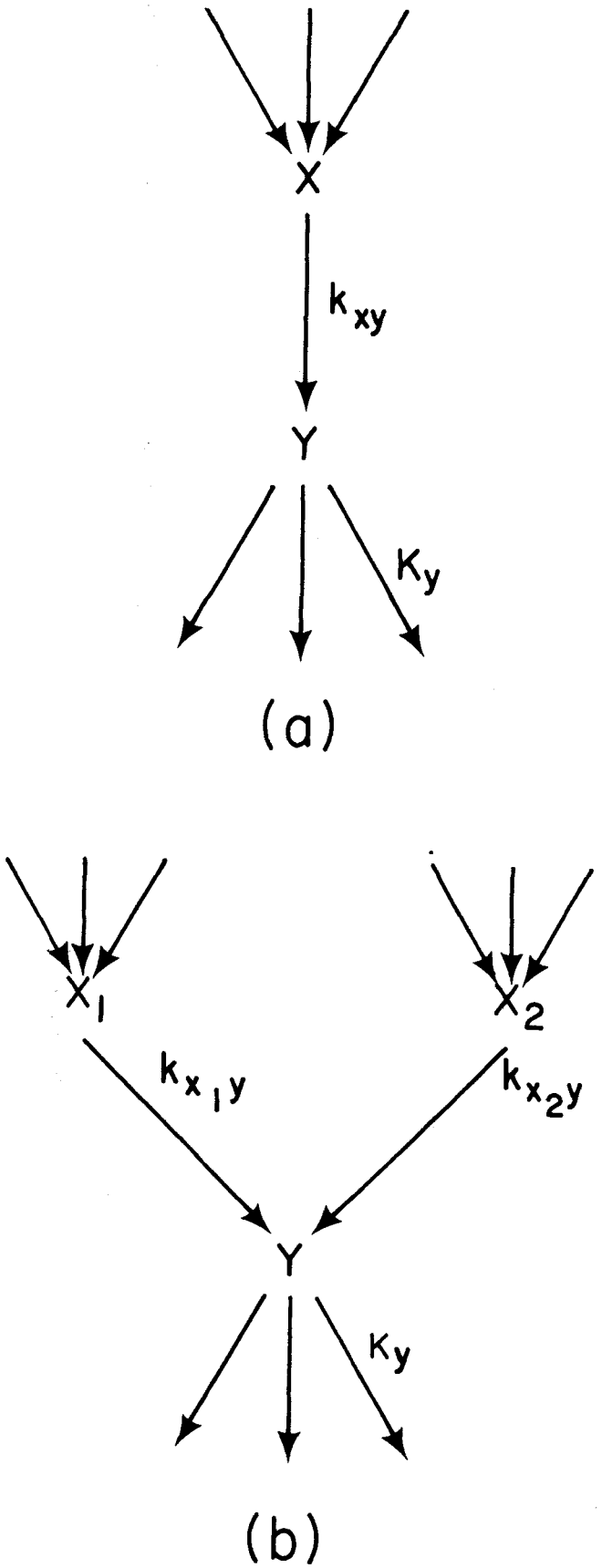


Fig. 4. Integral structure.

underlined. Applying rule 3, we note that lumps C and D are formed from initial lumps. Initial lump for lump C is denoted as I_1 and for lump D as I_2. If we apply rules 1, 4, and 5, and utilize the definition of a skeleton structure, results in Figure 3*b* are obtained. We note in Figure 3*b* that sum of the order of the source lumps for the formation of an n^{th}-order lump is $(n-1)$. The sum can exceed $(n-1)$. However, if the source lumps were independent of each other, the connection would have been wrong in such a case. A possible formation path for lump B from lump F was eliminated, since lump B has to be sixth order if lump F were to be connected to lump B. This is due to the fact that the source of lump F is either (I_1 and D) or (I_2 and C). Having obtained the structure in Figure 3*b*, we note that for lump H to be an eighth-order lump, there must be formation paths from lumps E and F. The structure shown in Figure 3*c* is a skeleton structure.

The skeleton structure of Figure 3*c* can be obtained from the eigenvalues given in Table 2. However, eigenvalues obtained from kinetic data would be numbers rather than symbols. Therefore, use of Table 2 should be deferred until after simple lumps are defined and a rough picture of the structure is known. Eigenvalues given in Table 2 can be used at a later stage of the synthesis for confirmation purpose, as can the elementary structures developed below.

3. Integral Structure

Consider an elementary structure shown in Figure 4. This is the case where there is only one path between two lumps (x and y). We have

$$\frac{dy}{dt} = k_{xy}W_{xy}x - K_y y \tag{3}$$

where K_y is the sum of all the rate constants associated with the disappearance reaction paths of lump y. Solving Equation (3) and rearranging the results, we have

$$\frac{y(t)}{\int_0^t e^{K_y\tau}x(\tau)\,d\tau} = k_{xy}W_{xy}e^{-K_y t} \tag{4}$$

Taking logarithm of both sides of the equation, we have

$$\ln\left\{\frac{y(t)}{\int_0^t e^{K_y\tau}x(\tau)\,d\tau}\right\} = \ln(k_{xy}W_{xy}) - K_y t \tag{5}$$

Equation (5) becomes a straight line with the slope of $-K_y$ and the intercept of $\ln(k_{xy}W_{xy})$ when the left-hand side of the equation is plotted against time. Therefore, if there exists only one path between two lumps, we would obtain a straight line as given by Equation (5). A special case of the elementary structure in Figure 4 is the case where there is no disappearance reaction path for lump y. In such a case, Equation (5) can be simplified to

$$y(t) = (k_{xy}W_{xy})\left(\int_0^t x(\tau)\,d\tau\right) \tag{6}$$

which is a straight line through origin with the slope of $k_{xy}W_{xy}$. The results can be easily extended to the case of two paths, and we have for the case in Figure 4*b*

$$\ln\left[\frac{y(t)}{\int_0^t e^{K_y\tau}\left[x_1 + \frac{k_{x2y}W_{x2y}}{k_{x1y}W_{x1y}}x_2\right]}\right] = \ln(k_{x1y}W_{x1y}) - K_y t \tag{7}$$

We state a rule resulting from the integral structure:

6. If Equation (5) yields a straight line, there is only one path between the lumps x and y. Furthermore, if the line goes through origin, the lump y is a lump with no disappearance reaction path. If Equation (7) yields a straight line, the lump y has only two reaction paths for the formation of y.

Similar results for three or more paths can be derived. However, inclusion of many lumps increases uncertainty in the results obtained. Furthermore, reduction of order n made possible by identifying exponential terms for the lower-order lumps would not require an expression for three or more paths. To apply Equation (5) to the experimental data on lumps x and y, assumed values of K_y are varied until a straight line is obtained. If an assumed value of K_y yields a straight line, there is only one path between the lumps x and y, and the rate constant K_y is obtained. Otherwise, no path exists between the two lumps. Similar procedures apply to Equation (7). A numerical illustration is given in Appendix B. Applying the rule 6 for the kinetic structure in Figure 1, we conclude that there exists only one formation path for lumps G and K and two paths for lump H. The results are summarized in Figure 3*d*. Lumps G, H, and K are circled to indicate that for those lumps, formation and disappearance paths are defined.

4. Derivative Structure

Consider an elementary structure shown in Figure 5. The rate expression for cases (a) and (b) are

$$\frac{dy}{dt} = k_{xy}W_{xy}x \qquad \text{for case (a)} \tag{8}$$

$$\frac{dy}{dt} = k_{xy}W_{xy}x + k_{Iy}W_{Iy}I \qquad \text{for case (b)} \tag{9}$$

Evaluating the derivatives at time zero, we have

$$\left.\frac{dy}{dt}\right|_{t=0} = 0 \qquad \text{for case (a)} \tag{10}$$

$$\left.\frac{dy}{dt}\right|_{t=0} = k_{Iy}W_{Iy}I_o \qquad \text{for case (b)} \tag{11}$$

where I_o is the initial concentration of an initial lump. The results show that if the first derivative for a lump

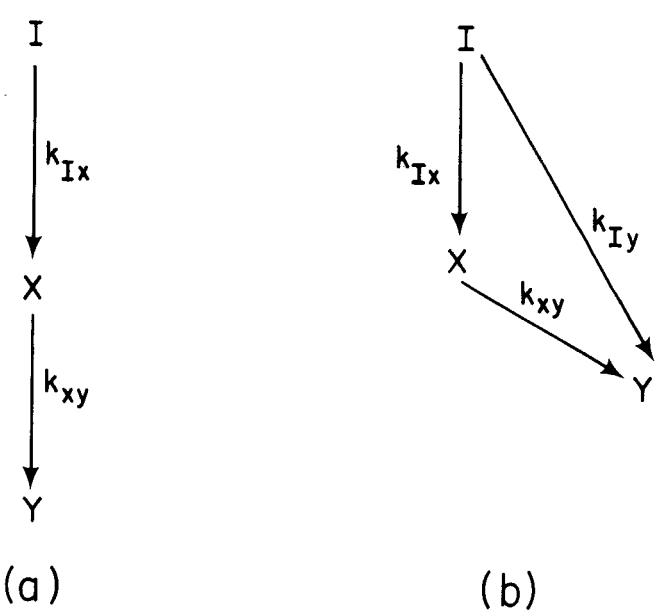


Fig. 5. Derivative structure.

TABLE 3

Lump	Possible source
B	I_1, I_2
F	(I_1 and D) or (I_2 and C)
E	I_1, I_2, C, D

TABLE 4

Lump	Possible source
B	I_1, I_2
E	I_1, I_2, C, D

evaluated at time zero is nonzero, there is at least one direct formation path for that lump from at least one initial lump. If the derivative is zero, there exists no direct formation path from initial lumps. Although the results are derived from a specific structure, it can be shown that the same results for any general case. We now state the following rule:

7. If the first-order derivative evaluated at time zero is nonzero for a lump, there is at least one direct path connecting that lump to an initial lump. If it is zero, there is no direct path from initial lumps to that lump.

In general, it is difficult to obtain accurate values of derivatives from experimental data. However, the derivatives obtained in the process of obtaining n and Q using Lee's method (1977) is rather accurate. Applying the rule 7 for the kinetic structure in Figure 1, we conclude that lumps B and E have at least one direct formation path from initial lumps I_1 and I_2.

We now list in Table 3 the source of formation reaction paths for each of the lumps whose formation/disappearance paths are yet to be defined.

5. Rate Constants

Only distinct rate constants corresponding to the eigenvalues of the characteristic equation of Equation (1) would be represented in a_i's [Equation (1)]. Values of a_i's determined from experimental data can be used to obtain values of distinct rate constants (Lee, 1977). If the distinct rate constants were obtained for the example in Figure 1, we would have eight of them as given in Table 2.

Consider lump F. If the source for the formation of F were I_1 and D, then the distinct rate constants of lump F should contain distinct rate constants of lumps I_1 and D. For the example considered (Figure 1), this would not be the case. Therefore, I_2 and C are the source for the formation of F. The results are shown in Figure 3*e*.

Information on individual rate constants such as k_{I1C}, k_{DB}, etc., in Figure 1 is contained in the initial conditions of higher than first-order derivatives of Equation (1) (Lee, 1977). Determination of individual rate constants from the initial conditions of derivatives would be quite difficult because of highly nonlinear nature if a lump is a higher-order lump. Therefore, we would first obtain individual rate constants associated with integral structure, starting with those lumps whose formation/disappearance paths are defined (circled lumps in Figure 3*e*). We can therefore determine without too much difficulty individual rate constants k_{EH}, k_{EG}, k_{I2F}, and k_{CF} (Figure 1) by utilizing the integral structure. Circled rate constants in Figure 1 are distinct rate constants and thus are known by now. For the low-order lumps C and D, the individual rate constants k_{I1C} and k_{I2D} can be easily determined.

We note that possible reaction paths are considerably reduced by now as given in Table 4. Acording to Table 4 and Figure 3*e*, there are at most four formation paths for lump B and five formation paths for lump E. Therefore, we would use the initial conditions of derivatives determined for lump B in determining individual rate constants, assuming that there are four formation paths for lump B. If the reaction mixture has the kinetic structure as given in Figure 1, none of the individual rate constants would assume zero value. Therefore, we have four formation reaction paths for lump B (Figure 3*f*).

To determine the existence of a reaction path from lump C to lump E, the value of K_c (Table 3) is compared with the sum of values of k_{CB} and k_{CF}, from which it can be concluded that there exists a reaction path. Similar reasoning leads to the existence of formation paths from I_1, I_2, and D. The final kinetic structure synthesized is given in Figure 3*g*.

Initial Lumps

Identifying kinetically consistent initial lumps is important. Initial lumps are kinetically consistent with a kinetic structure if all the kinetic constants determined from the kinetic structure are invariant with raw reactant compositions. This means that initial concentration of initial lumps in the raw reactant can vary, but the rate constants should not.

One of the objectives in synthesizing the kinetic structure in Figure 1 was to identify the initial lumps. As a result of the synthesis, we know that there are two initial lumps. Furthermore, we know the molecular weight of these lumps (most likely average molecular weight). Based on the information obtained, identity of the two initial lumps can be sought using chemical structure of raw reactant or physical properties such as density, boiling point, etc. Once the initial lumps are identified, the kinetic structure should be tested for its kinetic consistency. If the kinetic structure turns out to be kinetically inconsistent, kinetic lumps need to be added to the structure and the kinetic structure refined. We define kinetic lumps as the lumps added to the kinetic structure for kinetic consistency, even though these lumps are not products of interest. These kinetic lumps may or may not be measurable.

Concluding Remarks

Application of the theories developed to real processes would require trial and error and engineering judgments. Elementary structures such as integral structure should be first applied. Application of Equation (1) for the values of n, Q, and initial conditions of derivatives should be done first for those lumps that are likely to have order less than four. Once some of the distinct rate constants are determined, the order of the high-order lumps should be reduced using the distinct rate constants determined for the low-order lumps. Combinations of rules developed should be used as necessary to reduce the number of possibilities.

The synthesis method presented may or may not lead to a kinetically consistent kinetic structure. The real value of using the synthesis method is in reducing the number of possibilities to several kinetic structures that can be tested further. For instance, there could be conceivably 9^{10} possible kinetic structures for the ten lumps shown in Figure 1.

The synthesis method is also valuable in identifying the candidates for initial lumps. The initial lumps are not usually known, and yet proper selection of initial lumps is critical for any kinetic scheme of a reaction mixture to be useful and reliable. When the initial lumps are known, which is always the case when decomposition reactions of pure species are involved (Froment et al.,

1977), the synthesis method can be used with much ease for the kinetic structure of such a product mixture.

NOTATION

a_{nj} = constant in Equation (1) for j^{th} lump, a function of rate constants
I = initial lump or concentration of initial lump (moles/weight)
I_o = initial concentration of initial lump (moles/weight)
k_{ij} = rate constant for the reaction path from lump i to lump j (time^{-1})
K_y = overall rate constant in Equation (3)
L^{nj} = linear differential operator of n^{th}-order for lump j
P = product lump (A, B, C, D, E, F, G, H, K) or concentration of product lump (moles/weight)
Q_j = constant in Equation (1) for j^{th} lump
t = time
W_{ij} = molecular weight of lump i/molecular weight of lump j
x = concentration of lump x (moles/weight)
x_j = concentration of j^{th} lump in Equation (1) (moles/weight)
y = concentration of lump y (moles/weight)

LITERATURE CITED

Anthony, D. B., and J. B. Howard, "Coal Devolatilization and Hydrogasification," *AIChE J.*, **22**, 625 (1976).

Aris, R., "Prolegomena to the Rational Analysis of Systems of Chemical Reactions," *Arch. Pat. Hecm. Anal.*, **27**, 356 (1968).

———, and G. R. Gavalas, "Theory of Reactions in Continuous Mixtures," *Royal Soc. London Phil. Trans.*, **260**, 351 (1966).

Froment, G. F., B. O. Van de Steene, P. J. Van den Berghe, and A. G. Goosens, "Thermal Cracking of Light Hydrocarbons and Their Mixtures," *AIChE J.*, **2**, 93 (1977).

Golikeri, S. V., and D. Luss, "Aggregation of Many Coupled Consecutive First Order Reactions," *Chem. Eng. Sci.*, **9**, 845 (1974).

Jacob, S. M., B. Gross, S. E. Voltz, and V. W. Weekman, "A Lumping and Reaction Scheme for Catalytic Cracking," *AIChE J.*, **22**, 701 (1976).

Lee, H. H., "Kinetic Behavior of Mixtures with Many First-Order Reactions," *ibid.*, **23**, 116 (1977).

Luss, D., and P. Hutchinson, "Lumping of Mixtures with Many Parallel Nth Order Reactions," *Chem. Eng. J.*, **2**, 172 (1971).

———, and S. V. Golikeri, "Grouping of Many Species Each Consumed by Two Parallel First-Order Reactions," *AIChE J.*, **21**, 865 (1975).

Nace, D. M., S. E. Voltz, and V. W. Weekman, "Application of a Kinetic Model for Catalytic Cracking—Effects of Charge Stocks," *Ind. Eng. Chem. Process Design Develop.*, **10**, 530 (1971).

Ozawa, Y., "The Structure of a Lumpable Monomolecular System for Reversible Chemical Reactions," *Ind. Eng. Chem. Fundamentals*, **12**, 191 (1973).

Wei, J., and J. C. W. Kuo, "A Lumping Analysis in Monomolecular Reaction Systems," *ibid.*, **8**, 114 (1969).

APPENDIX A: Value of Q for Terminating Lumps

If a product lump is a terminating lump, Equation (2) can be simplified to

$$\frac{dP}{dt} = \sum_{i=1}^{m} W_{Ai} P \bar{k}_i A_i \qquad (A1)$$

Fig. B1. An illustration of application of integral structure.

Since A_i is a linear combination of exponentials of distinct rate constants, we can rewrite Equation (A1)

$$\frac{dP}{dt} = \sum_{j=1}^{n} a_i e^{-b_i t} \qquad (A2)$$

where b_i's are n distinct rate constants and a_i's are constants. Integrating Equation (A2), we have

$$P = \int_0^t \sum_{j=1}^{n} a_i e^{-b_i t}$$

$$= \sum_{j=1}^{n} \left(-\frac{a_i}{b_i}\right)(e^{-b_i t} - 1) \qquad (A3)$$

$$= -\sum_{j=1}^{n} \frac{a_i}{b_i} e^{-b_i t} + \sum_{j=1}^{n} \frac{a_i}{b_i}$$

Equation (A3) is the solution of an inhomogeneous nth order linear differential equation, which means that the value of Q in Equation (1) is nonzero.

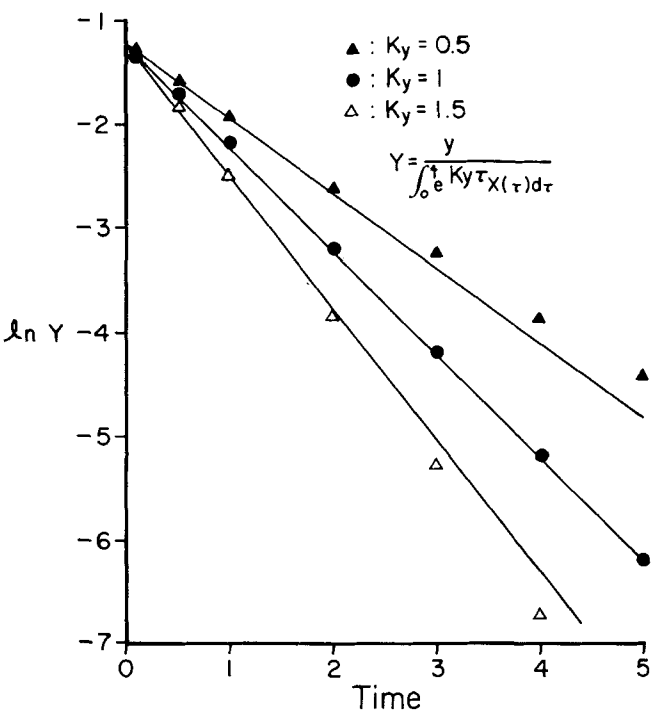
APPENDIX B: A Numerical Illustration of Application of Integral Structure

For the purpose of illustrating the application of Equation (5) to the integral structure of Figure 4(a), concentration of lumps x and y was calculated with the parameters given below:

$$x = 0.5e^{-0.2t}$$

$$k_{xy}W_{xy} = 0.3$$

$$K_y = 1.0$$



With the concentration of lumps x and y generated, left hand side of Equation (5) was calculated and plotted against time as shown in Figure B1 for different values of K_y assumed. The results in Figure 1 show that there is one reaction path connecting lump x to lump y and that the value of K_y is 1.0.

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