STOCHASTIC CHEMICAL REACTION WITH MOLECULAR DIFFUSION

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Report No. 212

August 1971

Abstract

Second-order, isothermal irreversible chemical reactions of single and two species in a homogeneous turbulent field are studied. Each case is divided into two parts, The first part, stochastically destributed chemical reaction (without diffusion), is designed to develop a workable closure which can be compared with the exact solution. In the second part, the closure developed in the first part is generalized to study reactions which are coupled with molecular diffusion.

For the very rapid reaction the approximation compares well with the exact solution as far as mean concentration and root mean square fluctuation of concentration are concerned, It predicts the skewness less satisfactorily.

For the rapid reaction, that is when the chemical kinetic reaction rate is greater than the molecular diffusion rate, molecular diffusion and initial fluctuations have a strong influence on the completeness of the reaction, However for the case that the molecular diffusion rate is greater than the reaction rate, neither diffusion nor initial fluctuations have much influence on the completeness of the reaction. These results agree with the observation that for a chemical kinetic reaction rate much greater than the molecular diffusion rate, reaction must depend on the molecular diffusion to bring the two reactants together before the reaction can start, When the kinetic reaction rate is much less than the molecular diffusion rate, the molecular diffusion always brings the two reactants together, and the time scale for completing the reaction is determined by the chemical kinetics.

For rapid second-order chemical reaction of two species with the same molecular diffusivity and stoichiometrically present in the system, O'Brien's theoretical analysis showed that both the mean and the root mean square fluctuation of a species concentration decay as $t^{-3/4}$ asymptotically and that the relative intensity of each species approaches a constant value of $\pi - 1$. Our closure predicts these asymptotic results quite well.

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Nomenclature

Letters

A, B	Species.
B(t)	Function defined by Eq. (3.53).
C	Chemical kinetic reaction rate constant.
C(k)	Function defined by Eq. (3.51).
C_1, C_2	Constant in Equations (2.8) and (2.9) respectively.
D	Molecular diffusivity.
EXP	Exponential.
f(x)	Function defined by Equations (2.35) and (3.62).
G(t)	Function defined by Eq. (3.54).
H(t)	Function defined by Eq. (3.56).
i	$\sqrt{-1}$.
$\underline{k}$	Vector in Fourier space.
k	Magnitude of vector $\underline{k}$.
L	Characteristic length; Integral scale of concentration.
n	Stoichiometric coefficient. (In Equations (2.6) and (3.9), n is an integer and indicates n-th moment.).
t	Time.
$\underline{u}$	The turbulent velocity field which is assumed to be incompressible, homogeneous and with zero mean.
U(t)	Function defined by Eq. (3.59a).
V(t)	Function defined by Eq. (3.60a).
w	Parameter of joint log-normal density function.

$\underline{x}$	Space distance vector.
x	Magnitude of vector $\underline{x}$.
y	variable of Equations (2.6) and (3.9).
Z	Function defined by Eq. (2.40).

Greek Symbols

α	$D_a/[Cn\overline{\Gamma_a}(0)L^2]$.
β	$\Gamma_b(0)/[n\overline{\Gamma_a}(0)]$.
Γ	Concentration.
Γ°	Normalized concentration, $\Gamma/\overline{\Gamma}(0)$.
γ	Concentration fluctuation,
ζ	Molecular diffusivity ratio, D_b/D_a.
η, ν	Parameters of the joint log-normal density function.
θ	Closure constant which is determined by the initial conditions.
λ	Microscale of concentration.
μ, σ	Parameters of the log-normal density function and the joint; log-normal density function.
ϕ	Fourier transform of $\overline{\gamma\gamma'}$.

Subscripts

a, b	Species.
j	Space distance component.

Superscripts

/	Indicates a space point some distance apart from the other reference point,
o	Dimensionless.
——	Ensemble average.

1. Introduction

Chemical reaction in a turbulent flow field is notoriously difficult to handle analytically even for the first order. This problem can be described by the mass conservation equation and the initial conditions. the three factors influencing the concentration field are turbulent convection, molecular diffusion, and chemical reaction. The influence of each factor was described by Corrsin[1]* and may be recalled:

It is empirically established that turbulent convection stretches the iso-concentration surface continuously on the average"..: By isopycnic mass conservation, this tends to bring surfaces ever closer together, i.e. to increase the scalar gradient fluctuation level. From the Fourier analysis view point this is propagation to higher and higher wave numbers in the spectrum of the concentration fluctuation field. Although the convective term in the mass conservation equation is linear, this particular behavior resembles that of a nonlinear phenomena.

The effect of molecular diffusion is to smear out these fluctuation gradients. The diffusion terms in the equation of conservation of mass cause no transfer through the spectrum, but they do discriminate against shorter wavelength because their effect is proportional to the spatial derivative rather than the fluctuation level itself.

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* Numbers in brackets designate bibliography at the end of the paper.

Little of a general nature can be said about the effect of chemical reaction terms on a homogeneous scalar fluctuation field because of the variety of function forms encountered for different reactions. Generally, the reaction rate between two components depend upon the concentrations of both. With a great excess of one, however, the rate expression can be approximated as a function of the other component only, $\phi(\Gamma)$. A number of chemical reaction rates are well approximated as a simple power of the local concentration, Γ^n, where n is called the order of reaction. For second-order reactions, the nonlinear reaction term must cause not only a loss in spectral content during flow out through wavenumber space (as does the first-order reaction) but also some additional spectral transfer [2].

During the past few years, people have studied this difficult problem with a variety of approximations and different methods of approach.

Toor and his colleagues [3], [4], [5] used the transformation first proposed by Burke and Schumann [6] to solve mathematically the limiting case of an instantaneous or diffusion-controlled reaction in such a way that the degree of completion of the reaction could be predicted by the use of data obtained from a mixing experiment carried out under identical hydrodynamic conditions. These predictions are in general agreement with measurements.

In 1958, Corrsin [1] solved one species reaction of first and second-order in an isotropic turbulence for the decay rates of mean concentration and fluctuation with some simplifying assumptions. The principal hypothesis introduced was that a first-order reaction has no effect on the size structure of the scalar field. He analyzed som'e limit cases without explicit consideration of the convective effect of the turbulence.

Lee [7] applied Kraichnan's direct interaction hypothesis [8] to both the convective term and the nonlinear concentration term of a one species chemical reaction. This analysis is only appropriate for' slow reactions. For the closures to yield consistent result with fast reactions, the initial mean concentration must be at least twice the root mean square concentration fluctuations since the direct interaction hypothesis in its present form is only applicable to concentraction fields of low initial relative intensity [9].

O'Brien has treated one species, very fast, stochastically distributed reactions of first and second order in his series of reports [10), [11], [12]. The 'convective and diffusion terms do not appear in these reactions. A closure, which satisfies initial and asymptotic conditions, for second-order reaction is proposed successfully. O'Brien [9] then used this closure approximation and proposed a statistical independence solution to the complete one species problem of combined reaction, turbulent convection, and molecular diffusion.

O'Brien, in another analysis [13], applied Kraichnan's

Lagrangian history direct interaction approximation to isotropic turbulent mixing of a second-order reaction. The resulting closed sets of equations were presented and an abridgement of them was carried out.

To date most theoretical work has been limited to cases of single species chemical reaction with the notable exceptions of Toor's analysis mentioned before, Pearson's [14] singular perturbation analysis of the diffusion of one reactant into a semi-infinite medium containing a second reactant with which it reacts according to a second-order equation, and O'Brien's [15] recent report of two species, very rapid, isothermal, irreversible, second-order, chemical reaction in a homogeneous turbulence. Some numerical models of two species reactions have recently appeared [16], [17].

It is the purpose of this paper to study two species second-orded reactions. The single species skcond-order reaction is also presented in the hope of developing a workable closure which can be easily generalized to the multispecies case as O'Brien's could not. We will follow O'Brien's idea of closure approximation which relates third moment to the first and second moments for the reaction term. The stochastically distributed reaction for both single and two species is studied in order to test the closure by comparing it with exact solutions which exist in analytical form.

In this preliminary closure analysis the explicit incorporation of turbulent convectian is not considered except to point out that in the limit of no molecular diffusion the turbulence plays no role in determing the decay of mean and root mean square concentrations of a homogeneous concentration field in a homogeneous turbulence [18]. This invariance must be satisfied. by any successful closure. It is automatically incorporated into the closures generated by the method developed here.

The following conditions are also assumed in order tc make the model simpler.

A. The concentration of the reactants and turbulence are assumed homogeneous and isotropic.

B. The chemical reaction is irreversible.

C. Any dynamic or chemical role that the product or products may play will be ignored.

d. The reaction rate "constant" and the molecular diffusivity are indeed constant in.space-time.

2. Second-Order Chemical Reaction of Single Species

Consider the isothermal, irreversible reaction of the type

$$A + A \longrightarrow \text{products} .$$

in an isotropic, homogeneous turbulence. The system as a second-order chemical reaction is described by the mass conservation equation

$$\frac{\partial \Gamma}{\partial t} + \cdot(\underline{u}\Gamma) \qquad \Gamma - c\Gamma^2 \tag{2.1}$$

The fluid is assumed incompressible, $\nabla \cdot \underline{u} = 0$.

The problem is made stochastic by assigning initial conditions in a statistical manner [11].

Following Corrsin [1] by defining $\bar{\Gamma}(t)$ as the mean and $\gamma(\underline{x},t)$ as the random fluctuation in concentration, the following relation holds [1] :

$$\frac{\partial \bar{\Gamma}}{\partial t} = -c(\bar{\Gamma}^2 + \overline{\gamma^2}) \tag{2.2}$$

$$\left(\frac{\partial}{\partial t} - 2D\frac{\partial^2}{\partial x_j \partial x_j}\right)\overline{\gamma\gamma'}(\underline{x},t) = -4c\bar{\Gamma}\,\overline{\gamma\gamma'}(\underline{x},t) - 2c\,\overline{\gamma^2\gamma'}(\underline{x},t) - 2\frac{\partial}{\partial x_j}\overline{u_j\gamma\gamma'}(\underline{x},t) \tag{2.3}$$

Where homogeneity has been used. The existence of triple fluctuation concentration moments in equation

(2.3) demonstrates the unclosed nature of the moment formulation and the necessity of resorting, in general, to approximation techniques.

2.1 Closure for Stochastically Distributed Single Species Reactions

For stochastically distributed reactions, that is those without turbulent convection or molecular diffusion but randomly distributed, the concentration field equations obeys (2.1) with $u = 0$ and $D = 0$

$$\frac{\partial \Gamma}{\partial t} = -C\Gamma^2 \tag{2.4}$$

Before analysing this situation we point out that for a very rapid reaction', $L^2 C\bar{\Gamma}(0)/D \gg 1$ and $LC\bar{\Gamma}(0)/\overline{u^2}^{\frac{1}{2}} \gg 1$ the concentration field will initially obey (2.4) up to a time significantly less than L^2/D or $L/\overline{u^2}^{1/2}$.

Let $t^\circ = C\bar{\Gamma}(0)t$, $\Gamma^\circ = \Gamma/\bar{\Gamma}(0)$ and drop the superscript°. Then (2.4) becomes

$$\frac{\partial \Gamma}{\partial t} = -\Gamma^2 \tag{2.5}$$

and it has the following solution [11]

$$\overline{\Gamma^n}(t) = \int_0^\infty \left(\frac{y}{1+yt}\right)^n p(y)\,dy \tag{2.6}$$

There are some asymptotic properties of (2.5) [12] which will play a role in checking the closure we will propose.

$$\lim_{t\to\infty} \overline{\Gamma} = t^{-1} \tag{2.7}$$

$$\lim_{t\to\infty} \overline{\gamma^2} = C_1 t^{-4} \tag{2.8}$$

$$\lim_{t\to\infty} \overline{\gamma^3} = -C_2 t^{-6} \tag{2.9}$$

The realizability conditions which we impose and which specify a certain degree of physical reasonableness to the solution are

$$0 \leq \overline{\Gamma}(t) < \infty \tag{2.10}$$

$$0 \leq \overline{\gamma^2}(t) < \infty \tag{2.11}$$

$$\overline{\gamma^3} > \frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma} \tag{2.12}$$

The inequality (2.12) arises from a restriction [19] on the skewness of any probability density which is zero for values of the random variable that are less than or equal to zero.

We propose the closure

$$\overline{\gamma^3} = (\theta - 1)\overline{\Gamma}\,\overline{\gamma^2} + (2\theta + 1)\frac{\overline{\gamma^2}^{\,2}}{\overline{\Gamma}} + \theta\frac{\overline{\gamma^2}^{\,3}}{\overline{\Gamma}^3} \tag{2.13}$$

Then

$$\overline{\gamma^3} - \left(\frac{\overline{\gamma^2}^2}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma}\right) = \theta\overline{\Gamma}\,\overline{\gamma^2} + 2\theta\frac{\overline{\gamma^2}}{\overline{\Gamma}} + \theta\frac{\overline{\gamma^2}^3}{\overline{\Gamma}^3}$$

so that (2.12) is satisfied if (2.10) and (2.11) are valid and $\theta \geq 0$.

From (2.5) and the closure (2.13), the differential equation for first and second moments of the concentration are

$$\frac{\partial\overline{\Gamma}}{\partial t} = -\left(\overline{\Gamma}^2 + \overline{\gamma^2}\right) \qquad (2.14)$$

$$\frac{\partial\overline{\gamma^2}}{\partial t} = -2\left[\theta\left(\overline{\Gamma} + 2\frac{\overline{\gamma^2}}{\overline{\Gamma}} + \frac{\overline{\gamma^2}^3}{\overline{\Gamma}^3}\right) + \frac{\overline{\gamma^2}}{\overline{\Gamma}} + \overline{\Gamma}\right]\overline{\gamma^2} \qquad (2.15)$$

From (2.15) we see that $\overline{\gamma^2} \geq 0$ and decreases to zero as t approaches infinity if $\theta \geq 0$. $\overline{\Gamma}$ can not be smaller than zero, because if it were than $\overline{\Gamma}=0$ at some time. From (2.15) $\overline{\gamma^2}/\overline{\Gamma}$ must be finite, this means that $\overline{\gamma^2}$ approaches zero before $\overline{\Gamma}$ does and remains at zero thereafter. Now, when $\overline{\Gamma}=0$ at some time, (2.14) would give $2\overline{\Gamma}/\partial t=0$. Therefore $\overline{\Gamma}=0$ thereafter. Therefore

$$\infty > \overline{\Gamma} \geq 0$$
$$\infty > \overline{\gamma^2} \geq 0$$

are satisfied.

From the above argument when t is very large the first term of the left hand side of Eq.(2.14) will be dominant, so that

$$\overline{\Gamma} \propto t^{-1}$$

and Eq.(2.15) gives

$$\overline{\gamma^2} \propto (2\theta + 1)\, t^{-2-2\theta}$$

and

$$\overline{\gamma^3} \propto (\theta - 1)\, t^{-3-2\theta} \qquad \text{if } \theta \neq 1$$

$$\propto (2\theta + 1)\, t^{-3-4\theta} \qquad \text{if } \theta = 1$$

O'Brien* [12] used two typical initial concentration distributions which give C_2 of (2.9) positive values and $\theta = 1.5$, 9/11 respectively.

For $\theta = 1.5$

$$\overline{\gamma^2} \propto t^{-5}$$

$$\overline{\gamma^3} \propto t^{-6}$$

$\overline{\gamma^2}$ drops faster than it should when t approaches infinity. The sign of $\overline{\gamma^3}$ is positive instead of negative when t approaches infinity.

For $\theta = 9/11$, $\overline{\gamma^2}$ and $\overline{\gamma^3}$ drop slower than they should but the signs are correct.

For log-normal initial concentration distributions+

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* see Eq. (2.31) and Eq. (2.32)

\+ see Eq. (2.33)

$\theta = 1$,

$$\overline{\gamma^2} \propto t^{-4}$$

$$\overline{\gamma^3} \propto t^{-7}$$

$\overline{\gamma^2}$ is asymptotic correct, but $\overline{\gamma^3}$ is incorrect asymptotically.

Therefore the closure may not predict accurately the asymptotic behavior of the mean square fluctuation and skewness. Fortunately, this is of little consequence as far as the mean concentration is concerned, because the limit to which all these quantities $\overline{\Gamma}$, $\overline{\gamma^2}$ and $\overline{\gamma^3}$ are tending is zero.

2.2 Closure for Stochastically Distributed Reactions with Molecular Diffusion

In this range of reaction system we need a closure for third moment of two space point, $\overline{\gamma^2\gamma}(\underline{x},t)$.

Neglect the turbulence term and (1.1) becomes:

$$\frac{\partial \Gamma}{\partial t} = D\,\nabla^2\Gamma - C\Gamma^2 \qquad (2.16)$$

Define the following dimensionless groups

$t^\circ = C\overline{\Gamma}(0)\,t$

$\Gamma^\circ = \Gamma/\overline{\Gamma}(0)$

$\underline{X}^\circ = \underline{X}/L$

$\alpha = D/C\overline{\Gamma}(0)L^2$

Equation (2.16) becomes

$$\frac{\partial \Gamma}{\partial t} = \alpha \nabla^2 \Gamma - \Gamma^2 \tag{2.17}$$

The realizability conditions (2.10) and (2.11) must be satisfied. Instead of (2.12), an inequality for $\overline{\gamma^3}$, another one arises [19]

$$\overline{\gamma^2\gamma'} > \frac{\overline{\gamma\gamma'}^2}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma} \tag{2.18}$$

We propose the closure

$$\overline{\gamma^2\gamma'}(\underline{x},t) = [\theta(\overline{\Gamma}+2\frac{\overline{\gamma^2}}{\overline{\Gamma}}+\frac{\overline{\gamma^2}^2}{\overline{\Gamma}}) - \overline{\Gamma} + \frac{\overline{\gamma^2}}{\overline{\Gamma}}]\,\overline{\gamma\gamma'}(\underline{x},t) \tag{2.19}$$

This reduces to (2.13) when $\underline{x} = 0$.

Then

$$\begin{aligned}\overline{\gamma^2\gamma'} - (\frac{\overline{\gamma\gamma'}^2}{\overline{\Gamma}} - \overline{\gamma^2}\,\overline{\Gamma}) &= \theta\overline{\Gamma}\,\overline{\gamma\gamma'} + \overline{\Gamma}(\overline{\gamma^2} - \overline{\gamma\gamma'}) \\ &+ 2\theta\,\frac{\overline{\gamma^2}\,\overline{\gamma\gamma'}}{\overline{\Gamma}} + \frac{\overline{\gamma\gamma'}}{\overline{\Gamma}}(\overline{\gamma^2} - \overline{\gamma\gamma'}) + \theta\,\frac{\overline{\gamma^2}^2\,\overline{\gamma\gamma'}}{\overline{\Gamma}^3}\end{aligned}$$

so that (2.19) is satisfied, if (2.10) and (2.11) are valid and

$$\theta \geq 0$$

$$\overline{\gamma^2} \geq \overline{\gamma\gamma'} \geq 0 \tag{2.20}$$

The differential equations for first and second moments of the concentration are from (2.17)

$$\frac{\partial \bar{\Gamma}}{\partial t} = -\left(\bar{\Gamma}^2 + \overline{\gamma^2}\right) \qquad (2.21)$$

$$\frac{\partial \overline{\gamma\gamma'}}{\partial t} + \left[-2\alpha\nabla^2 + 2\left\{(\theta+1)\bar{\Gamma} + (2\theta+1)\frac{\overline{\gamma^2}}{\bar{\Gamma}} + \theta\frac{\overline{\gamma^2}^2}{\bar{\Gamma}^3}\right\}\right]\overline{\gamma\gamma'} = 0 \qquad (2.22)$$

Where homogeneity has bean used, as has closure (2.19).

The Fourier transform of $\overline{\gamma\gamma'}(\underline{x},t)$ and its inverse are defined by

$$\phi(\underline{k},t) = \frac{1}{(2\pi)^3}\int_{\underline{x}} \overline{\gamma\gamma'}(\underline{x},t)\, \exp(-i\,\underline{k}\cdot\underline{x})\, d\underline{x} \qquad (2.23)$$

$$\overline{\gamma\gamma'}(\underline{x},t) = \int_{\underline{k}} \phi(\underline{k},t)\, \exp(i\,\underline{k}\cdot\underline{x})\, d\underline{k} \qquad (2.24)$$

By isotropy $\overline{\gamma\gamma'}(\underline{x},t)$ is a function of t and the magnitude of $\underline{x}$, say x, only, and $\phi(\underline{k},t)$ is a function of t and the magnitude of $\underline{k}$, say k, only. Therefore (2.23) and (2.24) reduce to

$$\phi(k,t) = \frac{1}{2\pi^2}\int_0^\infty \overline{\gamma\gamma'}(x,t)\, x^2\, \frac{\sin kx}{kx}\, dx \qquad (2.25)$$

$$\overline{\gamma\gamma'}(x,t) = 4\pi\int_0^\infty k^2\, \phi(k,t)\, \frac{\sin kx}{kx}\, dk \qquad (2.26)$$

Take the Fourier Transform of Eq. (2.22), we have

$$\frac{\partial \phi}{\partial t} + [2\alpha k^2 + 2\{(\theta+1)\overline{\Gamma} + (2\theta+1)\frac{\overline{\gamma^2}}{\overline{\Gamma}} + \theta\frac{\overline{\gamma^2}^2}{\overline{\Gamma}^3}\}]\phi = 0 \qquad (2.27)$$

The solution of Eq. (2.27) with an initial condition $\phi(k,0)$ is

$$\phi(k,t) = \phi(k,0)\,\mathrm{EXP}\{-2\alpha k^2 t - \int_0^t 2[(\theta+1)\overline{\Gamma} + (2\theta+1)\frac{\overline{\gamma^2}}{\overline{\Gamma}} + \theta\frac{\overline{\gamma^2}^2}{\overline{\Gamma}^3}]\,dt\} \qquad (2.28)$$

$$\overline{\gamma^2}(t) = 4\pi\int_0^\infty k^2\phi(k,0)\,\mathrm{EXP}(-2\alpha k^2 t)\,dk\;\mathrm{EXP}\{-\int_0^t 2[(\theta+1)\overline{\Gamma} + (2\theta+1)\frac{\overline{\gamma^2}}{\overline{\Gamma}} + \theta\frac{\overline{\gamma^2}^2}{\overline{\Gamma}^3}]\,dt\} \qquad (2.29)$$

$$\overline{\gamma\gamma'}(\underline{x},t) = 4\pi\int_0^\infty k^2\phi(k,0)\,\frac{\sin kx}{kx}\,\mathrm{EXP}(-2\alpha k^2 t)\,dk\;\mathrm{EXP}\{-\int_0^t 2[(\theta+1)\overline{\Gamma} + (2\theta+1)\frac{\overline{\gamma^2}}{\overline{\Gamma}} + \theta\frac{\overline{\gamma^2}^2}{\overline{\Gamma}^3}]\,dt\} \quad . \qquad (2.30)$$

since $\frac{\sin kx}{kx} \leq 1$, we **have**

$$\overline{\gamma^2} > \overline{\gamma\gamma'}$$

If $\overline{\gamma\gamma'} \geq 0$, then (2.20) **is** satisfied,

From (2.29), we ***see*** that $0 \leq \overline{\gamma^2}(t) < \infty$ ***is*** satisfied **if** $0 \leq \overline{\gamma^2}(0) < \infty$. $\overline{\gamma^2}$ **is a** decreasing function of *t* and *it* **decreases** faster than $\overline{\Gamma}$. Therefore, from (2.21)

$$\infty > \overline{\Gamma} \geq 0 \quad \text{if} \quad \infty > \overline{\Gamma}(0) \geq 0$$

2.3 Comparison of the Closure Solution with an Exact Solution for Stochastically Distributed Reactions of Single Species

In view of the relation (2.6), it is possible to compare the predictions of the closure with those obtained exactly when explicit initial probability distributions $P(\Gamma(0))$ of the concentration field are prescribed. We have carried out such a comparison with three typical distribution

$$P(y) = 60\, y^2 (1+y)^{-7} \qquad (2.31)$$

$$P(y) = (4.5)\,(3.5!)^{-1}\,(4.5\,y)^{3.5}\,\mathrm{EXP}\,(-4.5\,y) \qquad (2.32)$$

$$P(y) = \frac{1}{\sqrt{2\pi}\,\alpha y}\,\mathrm{EXP}\left(-\frac{[\ln y-\mu]^2}{2\alpha^2}\right) \qquad (2.33)$$

Where σ, μ are determined by the initial value $\overline{\Gamma}(0)$ or $\overline{\gamma^2}(0)$, since $\mathrm{T}^{\circ}(\sim)$ $\overline{\Gamma}(0)/\overline{\Gamma}(0) = 1$.

$$\sigma = \sqrt{\ln[1+\overline{\gamma^2}(0)]}$$

$$\mu = -\frac{1}{2}\ln[1+\overline{\gamma^2}(0)]\,.$$

With these forms of $P(\Gamma(0))$ it is possible to integrate (2.6), for example, by using Gaussian-Laguerre quadrature formulas [20]. These exact solutions are represented by fully inked in lines without a star * on Figs. 1-1 to 4-3. Figs. 1-1 to 1-3 are for distribution (2.31). Figs. 2-1 to 2-3 are for distribution (2.32). Figs. 3-1 to 4-3 are for distribution (2.33) with two different values of $\overline{\gamma^2}(0)$. θ is determined by the closure form (2.13) and the initial values computed from Eq. (2.6). Eqs. (2.21) and (2.22), with initial conditions $\overline{\Gamma}(0) = 1$ and $\overline{\gamma^2}(0)$, are solved numerically, for example, by using the Runge-Kutta Method [21]. $\overline{\gamma^3}$ is obtained by using closure (2.13). They are shown on Figs. 1-1 to 4-3 with stars on the lines. Table 1 lists both exact and approximate solutions for many different initial conditions at one particular t. With $\theta \geq 1$, as in the cases of distribution (2.31), (2.33), the closure gives $\overline{\gamma^3}$ always positive which is not a property of the exact solution, nevertheless for $\overline{\Gamma}$ and $\overline{\gamma^2}$ this is fair agreement with the exact solution.

O'Brien [12] used another kind of closure

$$\overline{\gamma^3} = A_1 \overline{\gamma^2}^2 \, \overline{\Gamma}^{-1} - A_0 \overline{\gamma^2}^2$$

and showed that there exist a maximum positive value of A_0, say A_{max}, such that for any $A_0 < A_{max}$ the closure satisfies all the asymptotic conditions and the realizability conditions. He then adjusted A_1, A_0 such that initial and asymptotic conditions are satisfied. The closure approximation prediction indeed agrees very well with the exact solution but the adjustment of A_1 and A_0 is a convenience not available in our case in which there is only one constant which is solely determined by the initial conditions.

Both O'Brien's and our closures give the same order of magnitude for mean and root mean square fluctuation of concentration with respect to the exact solution, but O'Brien's closure is more accurate on the prediction of skewness if the arbitrary constant is adjusted properly.

2.4 Application of the Closure for Stochastically Distributed Reactions of Single Species with Molecular Diffusion

As we pointed out in 2.2, we must know the initial correlation between two space point to solve this range of reaction systems.

As an example we assume

$$\overline{\gamma\gamma'}(x,0) = f(x)\,\overline{\gamma^2}(0) \qquad (2.34)$$

$$f(x) = \mathrm{EXP}\left(-\frac{x^2}{4}\pi\right) \qquad (2.35)$$

Where x, that is x^0, is dimensionless as defined in section 2.2. In terms of a variable x with a space dimension

$$f(x) = \mathrm{EXP}\left(-\frac{x^2}{4L^2}\pi\right)$$

Where L is an integral scale of the concentration fluctuation since

$$\int_0^\infty f(x)\,dx = L$$

Also since

$$\left.\frac{d^2f}{dx^2}\right)_{x=0} = -\frac{\pi}{2L^2} = -\frac{2}{\lambda^2}$$

Where λ is the microscale. We have

$$\lambda = \frac{2L}{\sqrt{\pi}}$$

Substituting (2.34) and (2.35) into (2.25), **we obtain**

$$\phi(k,0) = \frac{\overline{\gamma^2}(0)}{\pi^3}\,\mathrm{EXP}\left[-\frac{k^2}{\pi}\right] \qquad (2.36)$$

Equation (2.28) becomes

$$\phi(k,t) = \frac{\overline{\gamma^2}(0)}{\pi^3}\,\mathrm{EXP}\left[-\left(\frac{1}{\pi}+2\alpha t\right)k^2\right]\,\mathrm{EXP}\Big[-\int_0^t 2\Big\{(\theta+1)\bar{\Gamma} + (2\theta+1)\frac{\overline{\gamma^2}}{\bar{\Gamma}} + \theta\,\frac{\overline{\gamma^2}^2}{\bar{\Gamma}^3}\Big\}\,dt\Big] \qquad (2.37)$$

Equation *(2.29)* **becomes**

$$\overline{\gamma^2} = \frac{\overline{\gamma^2}(0)}{(1+2\pi\alpha t)^{3/2}}\,\mathrm{EXP}\left\{-\int_0^t 2\left\{(\theta+1)\bar{\Gamma} + (2\theta+1)\frac{\overline{\gamma^2}}{\bar{\Gamma}} + \theta\,\frac{\overline{\gamma^2}^2}{\bar{\Gamma}^3}\right]dt\right\} \qquad (2.38)$$

This would satisfy

$$0 \leq \overline{\gamma^2} < \infty$$

Equation (2.30) gives

$$\overline{\gamma\gamma'}(x,t) = \frac{\overline{\gamma^2}(0)}{(1+2\pi\alpha t)^{3/2}} \mathrm{EXP}\left[-\frac{\pi x^2}{4(1+2\pi\alpha t)}\right] \mathrm{EXP}\left\{-\int_0^t 2\left[(\theta+1)\overline{\Gamma}+(2\theta+1)\frac{\overline{\gamma^2}}{\overline{\Gamma}}+\theta\frac{\overline{\gamma^2}^2}{\overline{\Gamma}^3}\right]dt\right\} \tag{2.39}$$

Therefore

$$\overline{\gamma\gamma'}(x,t) > 0$$

From (2.21) and (2.38) we find $\overline{\Gamma}$ is a decreasing function of t and

$$\overline{\Gamma} \propto t^{-1}$$

so that

$$\infty > \overline{\Gamma} \geq 0$$

Inequality conditions (2.10), (2.11) and (2.18) are all satisfied.

Now let

$$Z = \int_0^t 2\left[(\theta+1)\overline{\Gamma}+(2\theta+1)\frac{\overline{\gamma^2}}{\overline{\Gamma}}+\theta\frac{\overline{\gamma^2}^2}{\overline{\Gamma}^3}\right]dt \tag{2.40}$$

$$\frac{dZ}{dt} = 2\left[(\theta+1)\overline{\Gamma}+(2\theta+1)\frac{\overline{\gamma^2}}{\overline{\Gamma}}+\theta\frac{\overline{\gamma^2}^2}{\overline{\Gamma}^3}\right] \tag{2.41}$$

Then (2.21) becomes

$$\frac{d\overline{\Gamma}}{dt} = -\overline{\Gamma}^2 - \frac{\overline{\gamma^2}(0)}{(1+2\pi\alpha t)^{3/2}} \mathrm{EXP}(-Z) \tag{2.42}$$

$$\frac{d\overline{\gamma^2}}{dt} = - \frac{\overline{\gamma^2}(0)}{(1+2\pi\alpha t)^{3/2}} \mathrm{EXP}(-Z) \left[-\frac{dZ}{dt} + \frac{3\pi\alpha}{(1+2\pi\alpha t)}\right] \quad (2.43)$$

Two initial conditions are given

$Z(0) = 0$

$\overline{\Gamma}(0) = 1$

For the sane initial conditions on single point quantities $\overline{\gamma^3}(0)$, $\overline{\gamma^2}(0)$, and $\overline{\Gamma}(0)$, θ has the same values in (2.19) as was determined by exact solutions in the 'previous use of the closure (2.1'3).

Again (2.41), (2.4 2), and (2.43) arc solved numerically by using Runge-Kutta Method [21] for several values of α, and the closure (2.13) gives $\overline{\gamma^3}$. Tho results are shown also in Figs, 1-1 to 4-3 and listed in Table 1. When α is order of 10 the greater α is the slower $\overline{\Gamma}$ decays, but when $\alpha > 10$, $\overline{\Gamma}$ does not; depend too strongly on α, For example, for a log-normal distribution, $\overline{\gamma^2}(0) = 2$, the maximum difference between $\overline{\Gamma}$ when $\alpha = 10$ and $\alpha = 100$ is only about 1.5 % up to dimensionless $t^0 = C\overline{\Gamma}(0)t = 2$, where the reaction is about 67 % completed. Also when $\alpha > 10$, the value of α and the type of the density function seem to have little effect on $\overline{\Gamma}$ up to $t^0 = 2$.

We expect that when diffusion phenomena is added into the reaction system the fluctuation will decay more rapidly. The closure indeed predicts this property satisfactorily.

3. Second-order Chemical Reaction of two Species

Consider the isothermal irreversible reaction of the type

$$A + n\,B \longrightarrow \text{products}$$

in isotropic, homogeneous turbulence. The system as a second-order chemical reaction is described by the mass conservation equations

$$\frac{\partial \Gamma_a}{\partial t} + \nabla \cdot (\underline{u}\,\Gamma_a) = D_a \nabla^2 \Gamma_a - c\,\Gamma_a \Gamma_b \qquad (3.1)$$

$$\frac{\partial \Gamma_b}{\partial t} + \nabla \cdot (\underline{u}\,\Gamma_b) = D_b \nabla^2 \Gamma_b - c\,n\,\Gamma_a \Gamma_b \qquad (3.2)$$

The fluid is assumed incompressible,

$$\nabla \cdot \underline{u} = 0$$

As in the single species if one tries to form the equations for the moments, the number of unknowns increase faster than the equations formed, Therefore, the approximation techniques have to be used again to close the system.

Define the following dimensionless groups:

$$\Gamma_a^\circ = \frac{\Gamma_a}{\overline{\Gamma_a}(0)}$$

$$\Gamma_b^\circ = \frac{\Gamma_b}{\overline{\Gamma_b}(0)}$$

$$t^\circ = c\,n\,\overline{\Gamma_a}(0)\,t$$

$$\underline{X}^\circ = \frac{X}{L}$$

$$u^{\circ} = \frac{\underline{u}}{C n \bar{\Gamma}_a(0) L}$$

$$\alpha = \frac{D_a}{C n \bar{\Gamma}_a(0) L^2}$$

$$\beta = \frac{\bar{\Gamma}_b(0)}{n \bar{\Gamma}_a(0)}$$

$$5 = \frac{D_b}{D_a}$$

After droping superscripts, (3.1) and (3.2) become

$$\frac{\partial \Gamma_a}{\partial t} + \nabla \cdot (\underline{u} \Gamma_a) = \alpha \nabla^2 \Gamma_a - \beta \Gamma_a \Gamma_b \qquad (3.3)$$

$$\frac{\partial \Gamma_b}{\partial t} + \nabla \cdot (\underline{u} \Gamma_b) = \alpha \xi \nabla^2 \Gamma_b - \Gamma_a \Gamma_b \qquad (3.4)$$

3. Second-Order Stochastically Distributed Chemical Reaction of two Species

For stochastically distributed reactants the kinetic equations are from (3.3) and (3.4)

$$\frac{\partial \Gamma_a}{\partial t} = -\beta \Gamma_a \Gamma_b \qquad (3.5)$$

$$\frac{\partial \Gamma_b}{\partial t} = -\Gamma_a \Gamma_b \qquad (3.6)$$

If the initial concentrations $\bar{\Gamma}_a(0)$, $\Gamma_b(0)$ are prescribed deterministically then the solution of (3.5) and (3.6) is

$$\Gamma_a(t) = \frac{\Gamma_a(0)\ \mathrm{EXP}\{[\Gamma_a(0) - \beta\Gamma_b(0)]\,t\}}{1 + \frac{\Gamma_a(0)}{\Gamma_a(0) - \beta\Gamma_b(0)}[\mathrm{EXP}\{\{\Gamma_a(0) - \beta\Gamma_b(0)\}\,t] - 1]} \qquad (3.7)$$

$$\Gamma_b(t) = \frac{\Gamma_a(0)\ \mathrm{EXP}\{[\Gamma_a(0) - \beta\Gamma_b(0)]\,t\}}{1 + \frac{\beta\Gamma_b(0)}{\beta\Gamma_b(0) - \Gamma_a(0)}[\mathrm{EXP}[\{\Gamma_a(0) - \beta\Gamma_b(0)\}\,t] - 1]} \qquad (3.8)$$

If the initial concentrations $\Gamma_a(0)$, $\Gamma_b(0)$ are prescribed stochastically in terms of a joint probability density, $P[\Gamma_a(0), \Gamma_b(0)]$, exact expressions for concentration moments **can** be derived as **following** :

$$\overline{\Gamma_a^n\Gamma_b^m} = \int_0^\infty\int_0^\infty \left[\frac{\xi\ \mathrm{EXP}\{(\xi - \beta\eta)t\}}{1 + \frac{\xi}{\xi - \beta\eta}\{\mathrm{EXP}[(\xi - \beta\eta)t] - 1\}}\right]^n \left[\frac{\xi\ \mathrm{EXP}\{(\xi - \beta\eta)t\}}{1 + \frac{\xi}{\xi - \beta\eta}\{\mathrm{EXP}[(\xi - \beta\eta)t] - 1\}}\right]^m p(\xi,\eta)\,d\xi\,d\eta \qquad (3.9)$$

As in **section** 2–1, the realizability conditions we impose which specify a certain degree of physical reasonableness to the solution are

$$0 \leq \overline{\Gamma}_a < \infty \qquad (3.10)$$

$$0 \leq \overline{\Gamma}_b < \infty \qquad (3.11)$$

$$0 \leq \overline{\gamma_a^2} < \infty \qquad (3.12)$$

$$0 \leq \overline{\gamma_b^2} < \infty \qquad (3.13)$$

$$\overline{\gamma_a^2\gamma_b} > \frac{\overline{\gamma_a\gamma_b}^2}{\overline{\Gamma}_b} - \overline{\Gamma}_b\,\overline{\gamma_a^2} \qquad (3.14)$$

$$\overline{\gamma_a\gamma_b^2} > \frac{\overline{\gamma_a\gamma_b}^2}{\overline{\Gamma}_a} - \overline{\Gamma}_a\,\overline{\gamma_b^2} \qquad (3.15)$$

We propose the closures

$$\overline{\gamma_a^2\gamma_b} = \left\{\theta\left[\overline{\Gamma}_a + \frac{\overline{\gamma_a^2}}{\overline{\Gamma}_a} + \frac{\overline{\gamma_a\gamma_b}}{\overline{\Gamma}_b} + \frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_a^2}}{\overline{\Gamma}_a^2\,\overline{\Gamma}_b}\right] - \overline{\Gamma}_a + \frac{\overline{\gamma_a^2}}{\overline{\Gamma}_a}\right\}\overline{\gamma_a\gamma_b} \tag{3.16}$$

$$\overline{\gamma_a} = \left\{\theta\left[\overline{\Gamma}_b + \frac{\overline{\gamma_b^2}}{\overline{\Gamma}_b} + \frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_b^2}}{\overline{\Gamma}_a\,\overline{\Gamma}_b^2} + \frac{\overline{\gamma_a\gamma_b}}{\overline{\Gamma}_a}\right] - \overline{\Gamma}_b + \frac{\overline{\gamma_b^2}}{\overline{\Gamma}_b}\right\}\overline{\gamma_a\gamma_b} \tag{3.17}$$

These closures seduce to closure (2.13) if species a and b are identical.

To see if (3.14) and (3.15) are satisfied, we have

$$\overline{\gamma_a^2\gamma_b} - \left(\frac{\overline{\gamma_a\gamma_b}^2}{\overline{\Gamma}_b} - \overline{\Gamma}_b\overline{\gamma_a^2}\right) = \overline{\Gamma}_b\overline{\gamma_a^2} - \overline{\Gamma}_a\overline{\gamma_a\gamma_b} + (\theta-1)\frac{\overline{\gamma_a\gamma_b}^2}{\overline{\Gamma}_b}$$
$$+\left\{\theta\left[\overline{\Gamma}_a + \frac{\overline{\gamma_a^2}}{\overline{\Gamma}_a} + \frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_a^3}}{\overline{\Gamma}_a^2\,\overline{\Gamma}_b}\right] + \frac{\overline{\gamma_a^2}}{\overline{\Gamma}_a}\right\}\overline{\gamma_a\gamma_b}$$

$$\overline{\gamma_a\gamma_b^2} - \left(\frac{\overline{\gamma_a\gamma_b}^2}{\overline{\Gamma}_a} - \overline{\Gamma}_a\overline{\gamma_b^2}\right) = \overline{\Gamma}_a\overline{\gamma_b^2} - \overline{\Gamma}_b\overline{\gamma_a\gamma_b} + (\theta-1)\frac{\overline{\gamma_a\gamma_b}^2}{4}$$
$$+\left\{\theta\left[\overline{\Gamma}_b + \frac{\overline{\gamma_b^2}}{\overline{\Gamma}_b} + \frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_b^2}}{\overline{\Gamma}_a\,\overline{\Gamma}_b}\right] + \frac{\overline{\gamma_b^2}}{\overline{\Gamma}_b}\right\}\overline{\gamma_a\gamma_b}$$

It is difficult to see that (3.14) and (3.15) are satisfied in general, but they can be proved for the special case that the joint probability density function of the initial concentrations $\Gamma_a(0)$, $\Gamma_b(0)$ is log-normal and $\theta = 1$. Therefore

$$\overline{\gamma_a^2\gamma_b} - \left(\frac{\overline{\gamma_a\gamma_b}}{\overline{\Gamma}_b} - \overline{\Gamma}_b\overline{\gamma_a^2}\right) = \frac{\overline{\gamma_a^2}}{\overline{\Gamma}_a^2\,\overline{\Gamma}_b}\left(\overline{\Gamma}_a\overline{\Gamma}_b + \overline{\gamma_a\gamma_b}\right)^2$$

$$\overline{\gamma_a\gamma_b^2} - \left(\frac{\overline{\gamma_a\gamma_b}^2}{\overline{\Gamma}_a} - \overline{\Gamma}_a\overline{\gamma_b^2}\right) = \frac{\overline{\gamma_b^2}}{\overline{\Gamma}_a\,\overline{\Gamma}_b^2}\left(\overline{\Gamma}_a\overline{\Gamma}_b + \overline{\gamma_a\gamma_b}\right)^2$$

and in this case if (3.10) to (3.13) arc valid, (3.14) and

(3.15) are satisfied by the closures (3.16) and (3.17).

Forming the first and second moment equations from (3.5) and (3.6) and using the closures (3.16) and (3.17), we obtain

$$\frac{\partial \bar{T}_a}{\partial t} = -\beta(\bar{T}_a \bar{T}_b + \overline{\gamma_a\gamma_b}) \tag{3.18}$$

$$\frac{\partial \bar{T}_b}{\partial t} = -(\bar{T}_a \bar{T}_b + \overline{\gamma_a\gamma_b}). \tag{3.19}$$

$$\frac{\partial \overline{\gamma_a^2}}{\partial t} = -2\beta[\theta(\frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_a^2}}{\bar{\bar{T}}_a^2\,\bar{\bar{T}}_b} + \frac{\overline{\gamma_a\gamma_b}}{\bar{\bar{T}}_b} + \frac{\overline{\gamma_a^2}}{\bar{\bar{T}}_a} + \bar{T}_a)\overline{\gamma_a\gamma_b} + \frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_a^2}}{\bar{\bar{T}}_a} + \bar{T}_b\overline{\gamma_a^2}] \tag{3.20}$$

$$\frac{\partial \overline{\gamma_b^2}}{\partial t} = -2[\theta(\frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_b^2}}{\bar{\bar{T}}_a\,\bar{\bar{T}}_b^2} + \frac{\overline{\gamma_a\gamma_b}}{\bar{\bar{T}}_a} + \frac{\overline{\gamma_b^2}}{\bar{\bar{T}}_b} + \bar{T}_b)\overline{\gamma_a\gamma_b} + \frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_b^2}}{\bar{\bar{T}}_b} + \bar{T}_a\overline{\gamma_b^2}] \tag{3.21}$$

$$\begin{aligned}\frac{\partial \overline{\gamma_a\gamma_b}}{\partial t} = &-[\theta(\frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_a^2}}{\bar{\bar{T}}_a^2\,\bar{\bar{T}}_b} + \frac{\overline{\gamma_a\gamma_b}}{\bar{\bar{T}}_b} + \frac{\overline{\gamma_a^2}}{\bar{\bar{T}}_a} + \bar{T}_a)\overline{\gamma_a\gamma_b} + \frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_a^2}}{\bar{\bar{T}}_a} + \bar{T}_b\overline{\gamma_a^2}] \\ &-\beta[\theta(\frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_b^2}}{\bar{\bar{T}}_a\,\bar{\bar{T}}_b^2} + \frac{\overline{\gamma_a\gamma_b}}{\bar{\bar{T}}_a} + \frac{\overline{\gamma_b^2}}{\bar{\bar{T}}_b} + \bar{T}_b)\overline{\gamma_a\gamma_b} + \frac{\overline{\gamma_a\gamma_b}\,\overline{\gamma_b^2}}{\bar{\bar{T}}_b} + \bar{T}_a\overline{\gamma_b^2}]\end{aligned} \tag{3.22}$$

Solutions of the above coupled equations depends on the initial data. As a specific example we will examine initial concentrations which are log-normally distributed, a possible distribution for non-negative random variables.

$$\begin{aligned}P(T_a(0), T_b(0)) = &\frac{1}{2\pi\,\sigma\,\eta\,T_a(0)\,T_b(0)\sqrt{1-w^2}}\,\mathrm{EXP}\{-[\frac{(\ln T_a(0)-\mu)^2}{2\sigma^2(1-w^2)} \\ &+ \frac{(\ln T_b(0)-\nu)^2}{2\eta^2(1-w^2)} - \frac{w(\ln T_a(0)-\mu)(\ln T_b(0)-\nu)}{\sigma\,\eta\,(1-w^2)}\end{aligned} \tag{3.23}$$

Where σ, η, μ, ν and w are determined by the initial conditions. Since $\overline{\Gamma_a}(0) = \overline{\Gamma_b}(0) = I$, we have

$$\sigma = [\ln(1 + \overline{\gamma_a^2}(0))]^{1/2}$$

$$\eta = [\ln(1 + \overline{\gamma_b^2}(0))]^{1/2}$$

$$\mu = -\frac{1}{2}\ln(1 + \overline{\gamma_a^2}(0))$$

$$\nu = -\frac{1}{2}\ln(1 + \overline{\gamma_b^2}(0))$$

We define a correlation coefficient ρ by

$$\rho = \frac{\overline{\gamma_a \gamma_b}(0)}{\overline{\gamma_a^2}(0)^{1/2}\ \overline{\gamma_b^2}(0)^{1/2}}$$

Then

$$W = \frac{1}{\eta\sigma} \ln\{\rho[\mathrm{EXP}(\sigma^2) - 1]^{1/2}[\mathrm{EXP}(\eta^2) - 1]^{1/2} + 1\}$$

So that *if* $\overline{\gamma_a^2}(0)$, $\gamma_b^2(0)$, $\overline{\gamma_a \gamma_b}(0)$ are specified, all the parameters in the density ffucntion $P(\Gamma_a(0), \Gamma_b(0))$ are provided.

Equation (3.9) in conjunction with (3.23) yields exact solutions for all moments. Figs. 5-1 to 8-5 are some of these exact solutions.

As we pointed out above, $\theta = 1$ for the log-normal distribution. (3.18) *to* (3.22) are solved with the same initial conditions as the exact solutions by using the

Runge-Kutta Method [21]. These closure solutions are shown by a line with * an the same figure as the corresponding exact solution, Table 2 lists both exact and approximate solutions at t = 10 for many different initial conditions.

3.2 Second-Order Chemical Reaction of two Species with Molecular Diffusion

In this range of reaction system with spatial correlations, we need closures for the third moments $\gamma_a \gamma_a' \gamma_b(\underline{x},t)$ and $\overline{\gamma_a \gamma_b \gamma_b'}(\underline{x},t)$.

Neglecting convective terms, (3.3) and (3.4) become

$$\frac{\partial \overline{\Gamma}_a}{\partial t} = \alpha \nabla^2 \overline{\Gamma}_a - \beta \overline{\Gamma}_a \overline{\Gamma}_b \tag{3.24}$$

$$\frac{\partial \overline{\Gamma}_b}{\partial t} = \alpha \xi \nabla^2 \overline{\Gamma}_b - \overline{\Gamma}_a \overline{\Gamma}_b \tag{3.25}$$

The realizability conditions (3.10) to (3.13) must be satisfied. We also require that (3.14) and (3.15) be satisfied.

We propose the closures

$$\overline{\gamma_a \gamma_a' \gamma_b} = \left[\theta\left(\overline{\Gamma}_a + \frac{\overline{\gamma_a^2}}{\overline{\Gamma}_a} + \frac{\overline{\gamma_a \gamma_b}}{\overline{\Gamma}_b} + \frac{\overline{\gamma_a \gamma_b}\,\overline{\gamma_a^2}}{\overline{\Gamma}_a^2 \overline{\Gamma}_b}\right) - \overline{\Gamma}_a\right] \overline{\gamma_a' \gamma_b} + \frac{\overline{\gamma_a \gamma_b}}{\overline{\Gamma}_a} \overline{\gamma_a \gamma_a'} \tag{3.26}$$

$$\overline{\gamma_a \gamma_b \gamma_b'} = \left[\theta\left(\overline{\Gamma}_b + \frac{\overline{\gamma_b^2}}{\overline{\Gamma}_b} + \frac{\overline{\gamma_a \gamma_b}}{\overline{\Gamma}_a} + \frac{\overline{\gamma_a \gamma_b}\,\overline{\gamma_b^2}}{\overline{\Gamma}_a \overline{\Gamma}_b^2}\right) - \overline{\Gamma}_b\right] \overline{\gamma_a \gamma_b'} - \frac{\overline{\gamma_a \gamma_b}}{\overline{\Gamma}_b} \overline{\gamma_b \gamma_b'} \tag{3.27}$$

These closures reduce to closures (3.16) and (3.17) when

$\underline{x} = 0$ and therefore automatically satisfy (3.14) and (3.15). By isotropy we have

$$\overline{\gamma_a'\gamma_a\gamma_b} = \overline{\gamma_a\gamma_a'\gamma_b} \qquad (3.28)$$

and

$$\overline{\gamma_a'\gamma_b'\gamma_b} = \overline{\gamma_a\gamma_b\gamma_b'} \qquad (3.29)$$

The following moment equations are formed from (3.24) and (3.25) by using closures (3.26), (3.27) and the conditions of isotropy and homogeneity.

$$\frac{\partial \overline{T}_a}{\partial t} = -\beta(\overline{T}_a\overline{T}_b + \overline{\gamma_a\gamma_b}) \qquad (3.30)$$

$$\frac{\partial \overline{T}_b}{\partial t} = -(\overline{T}_a\overline{T}_b + \overline{\gamma_a\gamma_b}) \qquad (3.31)$$

$$\frac{\partial\overline{\gamma_a\gamma_a'}}{\partial t} = 2\alpha\nabla^2\overline{\gamma_a\gamma_a'} + 2\theta\frac{\overline{\gamma_a'\gamma_b}}{\overline{T}_a^2\overline{T}_b}\frac{\partial\overline{T}_a}{\partial t}(\overline{\gamma_a^2} + \overline{}^2) + 2\frac{\overline{\gamma_a\gamma_a'}}{\overline{T}_a}\frac{\partial\overline{T}_a}{\partial t} \qquad (3.32)$$

$$\frac{\partial\overline{\gamma_b\gamma_b'}}{\partial t} = 2\alpha f\nabla^2\overline{\gamma_b\gamma_b'} + 2\theta\frac{\overline{\gamma_a'\gamma_b}}{\overline{T}_b^2\overline{T}_a}\frac{\partial\overline{T}_b}{\partial t}(\overline{\gamma_b^2} + \overline{T}_b^2) + 2\frac{\overline{\gamma_b\gamma_b'}}{\overline{T}_b}\frac{\partial\overline{T}_b}{\partial t} \qquad (3.33)$$

$$\begin{aligned}\frac{\partial\overline{\gamma_a'\gamma_b}}{\partial t} = {} & \alpha\nabla^2\overline{\gamma_a'\gamma_b} + \alpha f\nabla^2\overline{\gamma_a'\gamma_b} + \frac{\theta}{\beta}\frac{\overline{0\ \gamma_b}}{\overline{T}_a^2\overline{T}_b}\frac{\partial\overline{T}_a}{\partial t}(TT^2 + \overline{T}_a^2) \\ & + \frac{1}{\beta}\frac{\overline{\gamma_a\gamma_a'}}{\overline{T}_a}\frac{\partial\overline{T}_a}{\partial t} + \beta\theta\frac{,\overline{}}{\overline{T}_a^2\overline{T}_a}\frac{\partial\overline{T}_b}{\partial t}(\overline{\gamma_b^2} + \overline{T}_b^2) + \beta\frac{\overline{\gamma_b\gamma_b'}}{\overline{T}_b}\frac{\partial\overline{T}_b}{\partial t}\end{aligned} \qquad (3.34)$$

We define the Fourier transforms of $\overline{\gamma_a\gamma_a'}$, $\overline{\gamma_b\gamma_b'}$, $\overline{\gamma_a'\gamma_b}$ as in section 2.2. Equations (2.23), (2.24) and isotropy yield the results

$$\phi_{aa}(K,t) = \frac{1}{2\pi^2}\int_0^\infty \overline{\gamma_a\gamma_a'}(X,t)\, X^2 \frac{\sin KX}{KX}\, dX \qquad (3.35)$$

$$\phi_{bb}(K,t) = \frac{1}{2\pi^2}\int_0^\infty \overline{\gamma_b\gamma_b'}(X,t)\, X^2 \frac{\sin KX}{KX}\, dX \qquad (3.36)$$

$$\phi_{ab}(K,t) = \frac{1}{2\pi^2}\int_0^\infty \overline{\gamma_a'\gamma_b}(X,t)\, X^2 \frac{\sin KX}{KX}\, dX \qquad (3.37)$$

$$\overline{\gamma_a\gamma_a'}(X,t) = 4\pi\int_0^\infty K^2 \phi_{aa}(K,t)\, \frac{\sin KX}{KX}\, dK \qquad (3.38)$$

$$\overline{\gamma_b\gamma_b'}(X,t) = 4\pi\int_0^\infty K^2 \phi_{bb}(K,t)\, \frac{\sin KX}{KX}\, dK \qquad (3.39)$$

$$\overline{\gamma_a\gamma_b}(X,t) = 4\pi\int_0^\infty K^2 \phi_{ab}(K,t)\, \frac{\sin KX}{KX}\, dK \qquad (3.40)$$

Taking the Fourier transform of (3.32) to (3.34), we have

$$\frac{\partial\overline{\Gamma}_a}{\partial t} = -\beta\left[\overline{\Gamma}_a\overline{\Gamma}_b + 4\pi\int_0^\infty K^2\phi_{ab}(K,t)\, dK\right] \qquad (3.41)$$

$$\frac{\partial\overline{\Gamma}_b}{\partial t} = -\left[\overline{\Gamma}_a\overline{\Gamma}_b + 4\pi\int_0^\infty K^2\phi_{ab}(K,t)\, dK\right] \qquad (3.42)$$

$$\left(\frac{\partial}{\partial t} + 2\alpha K^2 - 2\frac{1}{\overline{\Gamma}_a}\frac{\partial\overline{\Gamma}_a}{\partial t}\right)\phi_{aa} = 2\theta\frac{\phi_{ab}}{\overline{\Gamma}_a^2\,\overline{\Gamma}_b}\frac{\partial\overline{\Gamma}_a}{\partial t}\left(\overline{\gamma_a^2} + \overline{\Gamma}_a^2\right) \qquad (3.43)$$

$$\left(\frac{\partial}{\partial t} + 2\alpha K^2\xi - 2\frac{1}{\overline{\Gamma}_b}\frac{\partial\overline{\Gamma}_b}{\partial t}\right)\phi_{bb} = 2\theta\frac{\phi_{ab}}{\overline{\Gamma}_a\,\overline{\Gamma}_b^2}\frac{\partial\overline{\Gamma}_b}{\partial t}\left(\overline{\gamma_b^2} + \overline{\Gamma}_b^2\right) \qquad (3.44)$$

$$\left[\frac{\partial}{\partial t} + \alpha\xi K^2 + \alpha K^2 - \frac{\theta}{\beta}\frac{1}{\overline{\Gamma}_a^2\,\overline{\Gamma}_b}\frac{\partial\overline{\Gamma}_a}{\partial t}\left(\overline{\gamma_a^2} + \overline{\Gamma}_a^2\right) - \beta\theta\frac{1}{\overline{\Gamma}_a\,\overline{\Gamma}_b^2}\frac{\partial\overline{\Gamma}_b}{\partial t}\left(\overline{\gamma_b^2} + \overline{\Gamma}_b^2\right)\right]\phi_{ab}$$
$$= \frac{\phi_{aa}}{\beta\overline{\Gamma}_a}\frac{\partial\overline{\Gamma}_a}{\partial t} + \beta\frac{\phi_{bb}}{\overline{\Gamma}_b}\frac{\partial\overline{\Gamma}_b}{\partial t} \qquad (3.45)$$

These five Equations, (3.41) to (3.45), with five unknowns could be solved in principal at least numerically, but it is difficult. As a simple example and in order to see the role that α plays. We will consider the case that A. Two reactants are presented stoichiometrically,

$\beta = 1.$

B. Species a and b are similarly distributed.

C. Diffusivities are the same, $\delta = 1$.

D. Initial concentrations of species a and b are jointly log-normally distributed, $\theta = 1$.

Then $\bar{\Gamma}_a = \bar{\Gamma}_b$ and (3.41) to (3.45) become

$$\frac{\partial \bar{\Gamma}_a}{\partial t} = -\left[\bar{\Gamma}_a \bar{\Gamma}_b + 4\pi \int_0^\infty k^2 \phi_{ab}(k,t)\, dk\right] \tag{3.46}$$

$$\left(\frac{\partial}{\partial t} + 2\alpha k^2 - 2\frac{1}{\bar{\bar{\Gamma}}_a}\frac{\partial \bar{\Gamma}_a}{\partial t}\right)\phi_{aa} = 2\frac{\phi_{ab}}{\bar{\bar{\Gamma}}_a^3}\frac{\partial \bar{\Gamma}_a}{\partial t}\left(\overline{\gamma_a^2} + \bar{\bar{\Gamma}}_a^2\right) \tag{3.47}$$

$$\left(\frac{\partial}{\partial t} + 2\alpha k^2 - 2\frac{1}{\bar{\bar{\Gamma}}_a}\frac{\partial \bar{\Gamma}_a}{\partial t}\right)\phi_{bb} = 2\frac{\phi_{ab}}{\bar{\bar{\Gamma}}_a^3}\frac{\partial \bar{\Gamma}_a}{\partial t}\left(\overline{\gamma_b^2} + \bar{\Gamma}_b^2\right) \tag{3.48}$$

$$\left[\frac{\partial}{\partial t} + 2\alpha k^2 - \frac{1}{\bar{\bar{\Gamma}}_a^3}\frac{\partial \bar{\Gamma}_a}{\partial t}\left(\overline{\gamma_a^2} + \overline{\gamma_b^2} + 2\bar{\bar{\Gamma}}_a^2\right)\right]\phi_{ab} = \frac{\phi_{aa} + \phi_{bb}}{\bar{\bar{\Gamma}}_a}\frac{\partial \bar{\Gamma}_a}{\partial t} \tag{3.49}$$

Combing (3.47), (3.48), and (3.49) we get

$$\frac{\partial}{\partial t}\left(\phi_{aa} + \phi_{bb} - 2\phi_{ab}\right) = -2\alpha k^2\left(\phi_{aa} + \phi_{bb} - 2\phi_{ab}\right)$$

Therefore

$$\phi_{ab} = \frac{1}{2}\left(\phi_{aa} + \phi_{bb}\right) - C(k)\, \mathrm{EXP}\left(-2\alpha k^2 t\right) \tag{3.50}$$

Where C(k) is determined from the initial spectrum as

$$2C(k) = \phi_{aa}(k,0) + \phi_{bb}(k,0) - 2\phi_{bb}(k,0) \qquad (3.51)$$

(3.41) becomes

$$\frac{\partial \overline{T}_a}{\partial t} = -\overline{T}_a^{\,2} - 2\pi\int_0^\infty k^2(\phi_{aa}+\phi_{bb})\,dk + 4\pi\int_0^\infty C(k)\,k^2\,\mathrm{EXP}(-2\alpha k^2 t)\,dk \qquad (3.52)$$

(3.47) plus (3.48), and the use of (3.50) and (3.52) gives

$$\frac{\partial}{\partial t}(\phi_{aa}+\phi_{bb}) + 2\Big\{\alpha k^2 - \frac{1}{\overline{T}_a}\frac{\partial \overline{T}_a}{\partial t} + \frac{1}{\overline{T}_a^{\,3}}\frac{\partial \overline{T}_a}{\partial t}\Big[\frac{\partial \overline{T}_a}{\partial t} - 4\pi\int_0^\infty C(k)k^2\,\mathrm{EXP}(-2\alpha k^2 t)\,dk\Big]\Big\}(\phi_{aa}+\phi_{bb}) = 4\frac{1}{\overline{T}_a^{\,3}}\frac{\partial \overline{T}_a}{\partial t}C(k)\,\mathrm{EXP}(-2\alpha k^2 t)\Big[\frac{\partial \overline{T}_a}{\partial t} - 4\pi\int_0^\infty C(k)\,k^2\,\mathrm{EXP}(-2\alpha k^2 t)\,dk\Big]$$

Let

$$B(t) = \int_0^\infty C(k)\,k^2\,\mathrm{EXP}(-2\alpha k^2 t)\,dk$$

$$= \frac{1}{2}\int_0^\infty k^2[\phi_{aa}(k,0) + \phi_{bb}(k,0) - 2\phi_{ab}(k,0)]\,\mathrm{EXP}(-2\alpha k^2 t)\,dk \qquad (3.53)$$

$$G(t) = \frac{1}{\overline{T}_a^{\,3}}\frac{\partial \overline{T}_a}{\partial t}\Big[\frac{\partial \overline{T}_a}{\partial t} - 4\pi B(t)\Big] \qquad (3.54)$$

then

$$\phi_{aa} + \phi_{bb} = 4\,\overline{T}_a^{\,2}\,\mathrm{EXP}\Big[-2\alpha k^2 t - 2\int_0^t G(t)\,dt\Big]\Big[\int_0^t C(k)\,\mathrm{EXP}\Big\{2\int_0^t G(t)\,dt\Big\}\frac{G(t)}{\overline{T}_a^{\,2}}\,dt + \frac{1}{4}\{\phi_{aa}(k,0) + \phi_{bb}(k,0)\}\Big] \qquad (3.55)$$

Let

$$H(t) = \int_0^\infty k^2\,\mathrm{EXP}(-2\alpha k^2 t)\,[\phi_{aa}(k,0) + \phi_{bb}(k,0)]\,dk \qquad (3.56)$$

Substituting (3.55) and (3.56) into (3.52)

$$\frac{\partial \overline{T}_a}{\partial t} = -\overline{T}_a^2 + 4\pi B(t) - \overline{T}_a^2 \, \mathrm{EXP}\left[-2\int_0^t G(t)\,dt\right]$$

$$\left\{8\pi B(t)\int_0^t \frac{G(t)}{\overline{T}_a^2}\,\mathrm{EXP}\left[2\int_0^t G(t)\,dt\right] + 2\pi H(t)\right\} \quad (3.57)$$

Let

$$U(t) = \mathrm{EXP}[-2\int_0^t G(t)\,dt \quad (3.59a)$$

$$V(t) = \int_0^t \frac{G(t)}{U(t)\,\overline{T}_a^2(t)}\,dt \quad (3.60a)$$

Finally we have the following system of first-order ordinary differential equations and the initial conditions :

$$\frac{\partial \overline{T}_a}{\partial t} = -\overline{T}_a^2 + 4\pi B(t) - 2\pi \overline{T}_a^2 U(t)\left[4B(t)V(t) + H(t)\right] \quad (3.58)$$

$$\frac{\partial U(t)}{\partial t} = -2G(t)U(t) \quad (3.59)$$

$$\frac{\partial V(t)}{\partial t} = G(t)/\overline{T}_a^2/U(t) \quad (3.60)$$

$$\overline{T}_a(0) = 1$$

$$U(0) = 1 \quad (3.61)$$

$$V(0) = 0$$

where B(t), G(t), H(t) are defined by Equations (3.53), (3.54), and (3.56) respectively. B(t) and H(t) are known functions of t provided that the initial spectra functions

$\phi_{aa}(k,0)$, $\phi_{bb}(k,0)$, and $\phi_{ab}(k,0)$ are given; or alternatively, the initial. correlation of reactants $\overline{\gamma_a\gamma_a'}(x,0)$, $\overline{\gamma_a'\gamma_b}(x,0)$, and $\overline{\gamma_b\gamma_b'}(x,0)$ are known.

If the reactants a and b are similarly distributed, we may assume, for example,

$$\overline{\gamma_a\gamma_a'}(x,0) = f(x)\,\overline{\gamma_a^2}(0)$$

$$\overline{\gamma_b\gamma_b'}(x,0) = f(x)\,\overline{\gamma_b^2}(0)$$

$$\overline{\gamma_a'\gamma_b}(x,0) = \rho f(x)\,\overline{\gamma_a^2}(0)^{1/2}\,\overline{\gamma_b^2}(0)^{1/2}$$

Where

$$|f(x)| \le 1 \;, \quad f(0) = 1$$

$$\rho = \frac{\overline{\gamma_a\gamma_b}(0,0)}{\overline{\gamma_a^2}(0)^{1/2}\,\overline{\gamma_b^2}(0)^{1/2}}$$

As ad example, using the same correlation function f(x) as in (2.35)

$$f(x) = \mathrm{EXP}\left(-\frac{x^2}{4}\pi\right) \qquad (3.62)$$

the following relations are obtained.

$$\phi_{aa}(k,0) = \frac{\overline{\gamma_a^2}(0)}{\pi^3}\,\mathrm{EXP}\left\{-\frac{k^2}{\pi}\right\}$$

$$\phi_{bb}(k,0) = \frac{\overline{\gamma_b^2}(0)}{\pi^3}\,\mathrm{EXP}\left\{-\frac{k^2}{\pi}\right\}$$

$$\phi_{ab}(k,0) = \frac{\rho\, \overline{\gamma_a^2(0)}^{1/2}\, \overline{\gamma_b^2(0)}^{1/2}}{\pi^3} \, \mathrm{EXP}\left(-\frac{k^2}{\pi}\right)$$

$$C(k) = \frac{1}{2\pi^3}\left[\overline{\gamma_a^2(0)} + \overline{\gamma_b^2(0)} - 2\rho\, \overline{\gamma_a^2(0)}^{1/2}\, \overline{\gamma_b^2(0)}^{1/2}\right] \mathrm{EXP}\left(-\frac{k^2}{\pi}\right)$$

$$B(t) = \frac{\overline{\gamma_a^2(0)} + \overline{\gamma_b^2(0)} - 2\rho\, \overline{\gamma_a^2(0)}^{1/2}\, \overline{\gamma_b^2(0)}^{1/2}}{8\pi\,(1+2\pi\alpha t)^{3/2}}$$

$$H(t) = \frac{\overline{\gamma_a^2(0)} + \overline{\gamma_b^2(0)}}{4\pi\,(1+2\pi\alpha t)^{3/2}}$$

(3.58) to (3.60) become

$$\frac{\partial \bar{\Gamma}_a}{\partial t} = -\bar{\Gamma}_a^2 + \frac{\overline{\gamma_a^2(0)} + \overline{\gamma_b^2(0)} - 2\rho\, \overline{\gamma_a^2(0)}^{1/2}\, \overline{\gamma_b^2(0)}^{1/2}}{2\,(1+2\pi\alpha t)^{3/2}} - \bar{\Gamma}_a^{-2} U$$
$$\left[V\, \frac{\overline{\gamma_a^2(0)} + \overline{\gamma_b^2(0)} - 2\rho\, \overline{\gamma_a^2(0)}^{1/2}\, \overline{\gamma_b^2(0)}^{1/2}}{(1+2\pi\alpha t)^{3/2}} + \frac{\overline{\gamma_a^2(0)} + \overline{\gamma_b^2(0)}}{2\,(1+2\pi\alpha t)^{3/2}}\right] \quad (3.63)$$

$$\frac{\partial U}{\partial t} = -2\, \frac{U}{\bar{\Gamma}^3}\, \frac{\partial \bar{\Gamma}}{\partial t}\left[\frac{\partial \bar{\Gamma}_a}{\partial t} - \frac{\overline{\gamma_a^2(0)} + \overline{\gamma_b^2(0)} - 2\rho\, \overline{\gamma_a^2(0)}^{1/2}\, \overline{\gamma_b^2(0)}^{1/2}}{2\,(1+2\pi\alpha t)^{3/2}}\right] \quad (3.64)$$

$$\frac{\partial V}{\partial t} = \frac{1}{U(t)\,\bar{\Gamma}_a^5}\, \frac{\partial \bar{\Gamma}_a}{\partial t}\left[\frac{\partial \bar{\Gamma}_a}{\partial t} - \frac{\overline{\gamma_a^2(0)} + \overline{\gamma_b^2(0)} - 2\rho\, \overline{\gamma_a^2(0)}^{1/2}\, \overline{\gamma_b^2(0)}^{1/2}}{2\,(1+2\pi\alpha t)^{3/2}}\right] \quad (3.65)$$

These first order system of ordinary differential equations are solved with the initial conditions (3.61) by the Runge-Kutta Method [21].

Now the fluctuations are

$$\frac{\overline{\gamma_a^2} + \overline{\gamma_b^2}}{2} = 4\pi \int_0^{\infty} k^2\, \frac{\phi_{aa} + \phi_{bb}}{2}\, dk$$
$$= U(t)\, \bar{\Gamma}_a^2 \left[\frac{V \{\overline{\gamma_a^2(0)} + \overline{\gamma_b^2(0)} - 2\rho\, \overline{\gamma_a^2(0)}^{1/2}\, \overline{\gamma_b^2(0)}^{1/2}}{(1+2\pi\alpha t)^{3/2}} + \frac{\overline{\gamma_a^2(0)} + \overline{\gamma_b^2(0)}}{2\,(1+2\pi\alpha t)^{3/2}}\right]$$
(3.66)

$$\overline{\gamma_a \gamma_b} = \frac{\overline{\gamma_a^2} + \overline{\gamma_b^2}}{2} - \frac{\overline{\gamma_a^2(0)} + \overline{\gamma_b^2(0)} - 2\rho\, \overline{\gamma_a^2(0)}^{1/2}\, \overline{\gamma_b^2(0)}^{1/2}}{2\,(1+2\pi\alpha t)^{3/2}} \qquad (3.57)$$

These results are shown on Figs. (5-1) to (7-3) as corresponding cases (same initial conditions) of reaction in section 3.1, and also listed on Table 2.

The numerical calculations are carried out with $\overline{\gamma_a^2}(0)$ varying from 0.5 to 2, $\overline{\gamma_b^2}(0)$ varying from 0.5 to 2, and the initial coefficient of correlation from 0 to 0.7 (or parameter w of the log-normal density function varying from 0 to 0.75). $\overline{\gamma_a^2} + \overline{\gamma_b^2}$ is non-negative for all time as it should be.

For the rapid reactions, that is when α is small, diffusion and initial fluctuations have a strong influence on the completeness of the reaction, but for the case that the diffusion rate is greater than the reaction rate (α is large), neither diffusion nor initial fluctuations have much influence on the completeness of the reaction. For example, with α varying from 5 to 100, the reaction is about 90.7 % completed in a dimensionless time t^o, defined as $Cn\overline{\Gamma_a}(0)t$, of 10 for all the possible combinations of the parameters described in the preceding paragraph, and the maximum difference of all these cases up to $t^o = 10$ is no more than 0.25 %.

These results are expected, since for a reaction rate (chemical kinetic) much greater than the molecular diffusion rate, reaction must depend on molecular diffusion to bring the two reactants together before the reaction can start. When the kinetic reaction rate is much less than the molecular diffusion, the molecular diffusion always brings the two reactants together and the time scale for completing the reaction is determined by the chemical kinetics.

For the rapid reaction with the same molecular diffusivity and the reactants stoichiometrically present in the system, O'Brien [22] showed that both the mean and the root mean square fluctuation of a species concentration decay as $t-3/4$ asymptotically and that the relative intensity of each species approaches a constant value, $(\pi - 1)$. These results are checked by carrying out the calculation, up to a time substantially greater than the time that diffusion becomes significant, for the case of initial concentration fluctuations, $\overline{\gamma_a^2}(0) = \overline{\gamma_b^2}(0) = 2$, and $w = 0.75$, $\alpha = 0.01$. The dimension time for diffusion to become significant is

$$t = O(L^2 / D_a)$$

or

$$t^o = O(\alpha^{-1})$$

The calculations are extended to $t^o = 2400$, these are well into the asymptotic regime for which the theory is applicable, although the theory is only exact for an asymptotically small α.

The results are shown on Figures 9 and 10, and are approximately as following :

$$\overline{\gamma_a^2}^{1/2} \propto t^{-0.74}$$

$$\overline{\Gamma} \propto t^{-0.83}$$

$$\overline{\gamma_a^2}\,\overline{\Gamma}^{-2} \propto 0(10)$$

4. Dicussion

In the study of two species chemical reactions the diffusivities of the species are assumed equal and the reactants stoichiometrically present. When the reaction rate is less than the molecular diffusion rate, the decay of the mean concentration depends only weakly on the diffusivity. In this case we may assume diffusivities of each species are equal even they are actually not, so that the above analysis may be used to predict the completeness of reaction.

When the reaction rate is the same order as or greater than molecular diffusion rate, the later plays an important role, and it is difficult to justify assuming that diffusivities of each species are equal if they are actually not. This case and the case when the reactants are not stoichiometrically present can be solved in principle by using Eqs. (3.41) to (3.45).

Solutions for second-order chemical reaction exist for the rapid diffusion controlled reaction [3], [4], [5], but there is no solutions to the cases that chemical kinetic reaction rate and molecular diffusion rate are the same order. Our closure technique is the only existing method based on the kinetic equations of solving for this situation, i. e. $\lambda = O(1)$.

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Symbols used on Figures 1-1 to 8-5

Exact solution : $\alpha = 0$	———————
Approximation solution :	
$\alpha = 0$	—*——*—
$\alpha = 0.01$	△
$\alpha = 1$	•
$\alpha = 10$	+
$\alpha = 100$	X

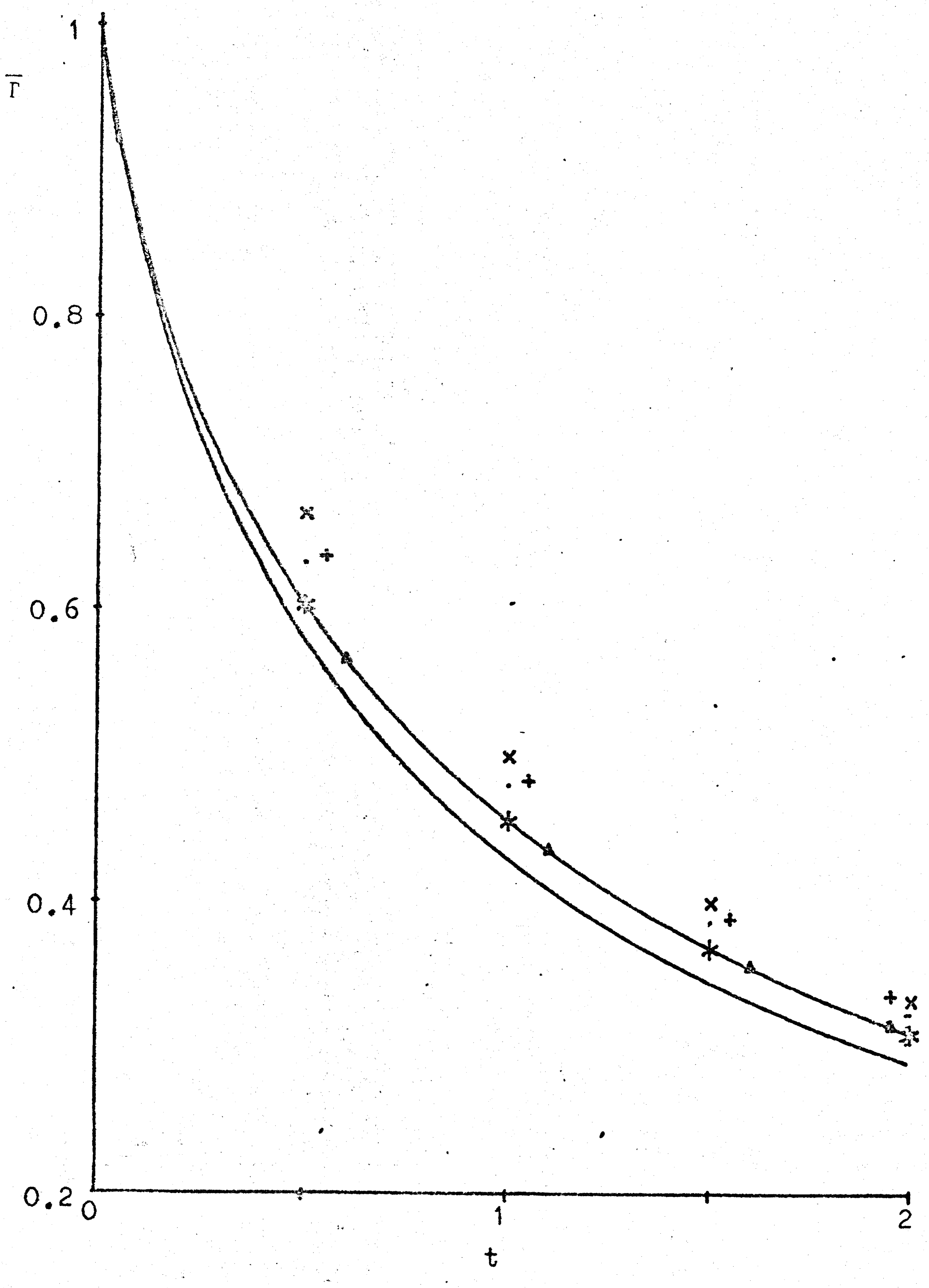

Fig.1-1. Normalized mean concentration vs. dimensionless time for probability distribution Eq. (2.51)

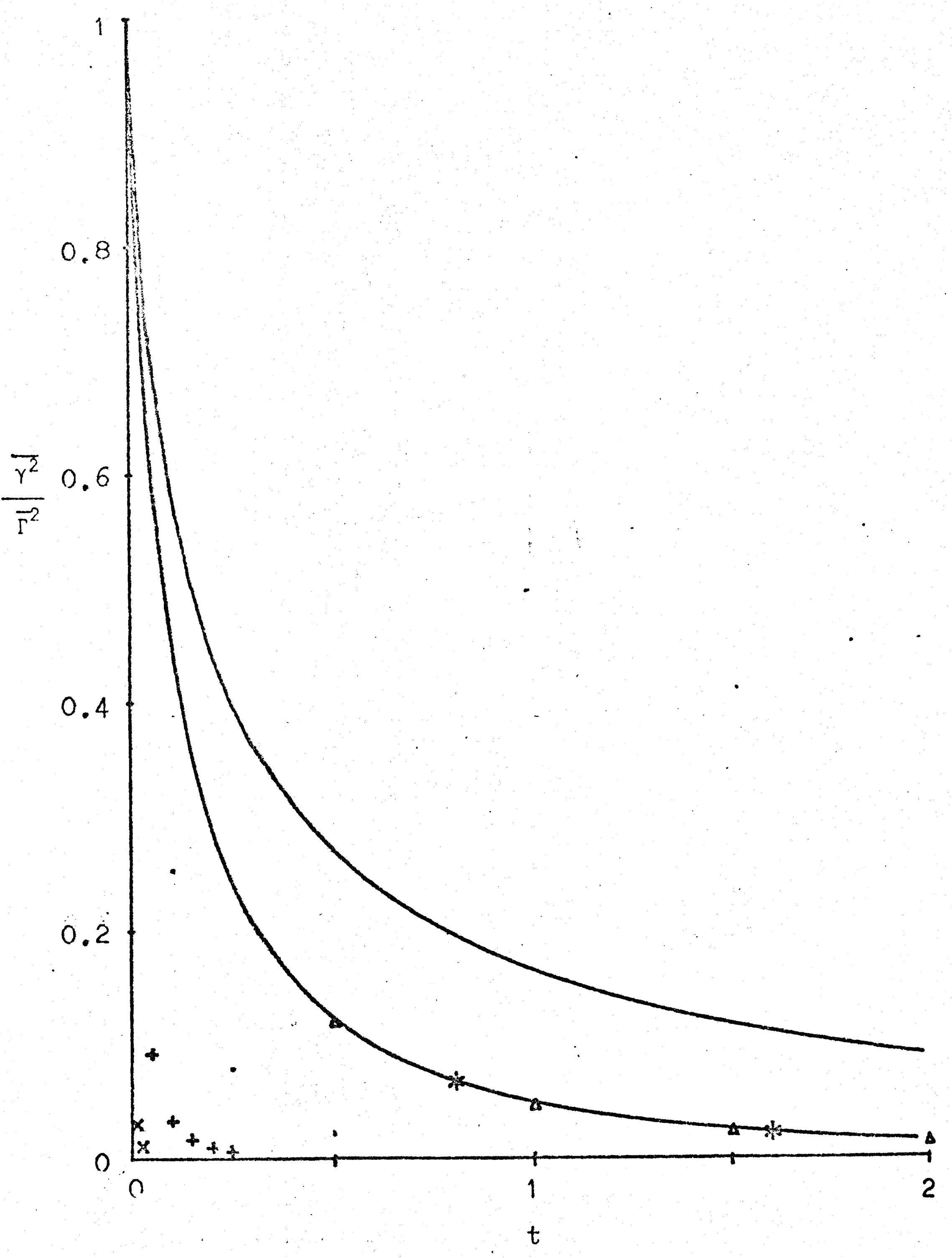

Fig. 1-2. Concentration relative intensity vs. dimensionless time for probability distribution Eq. (2.31)

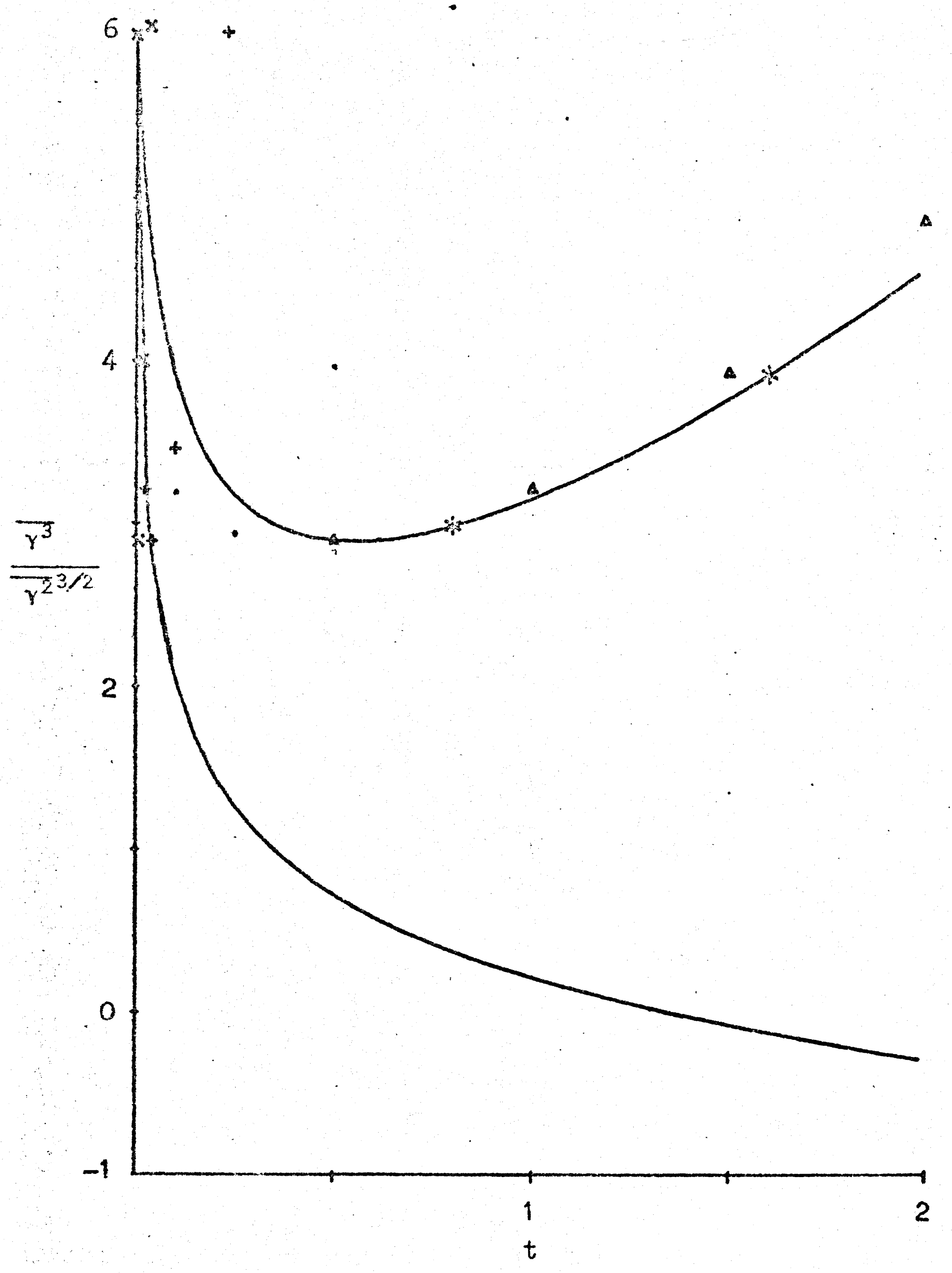

Fig. 1-3. Concentration skewness vs. dimensionless time for probability distribution Eq. (2.31)

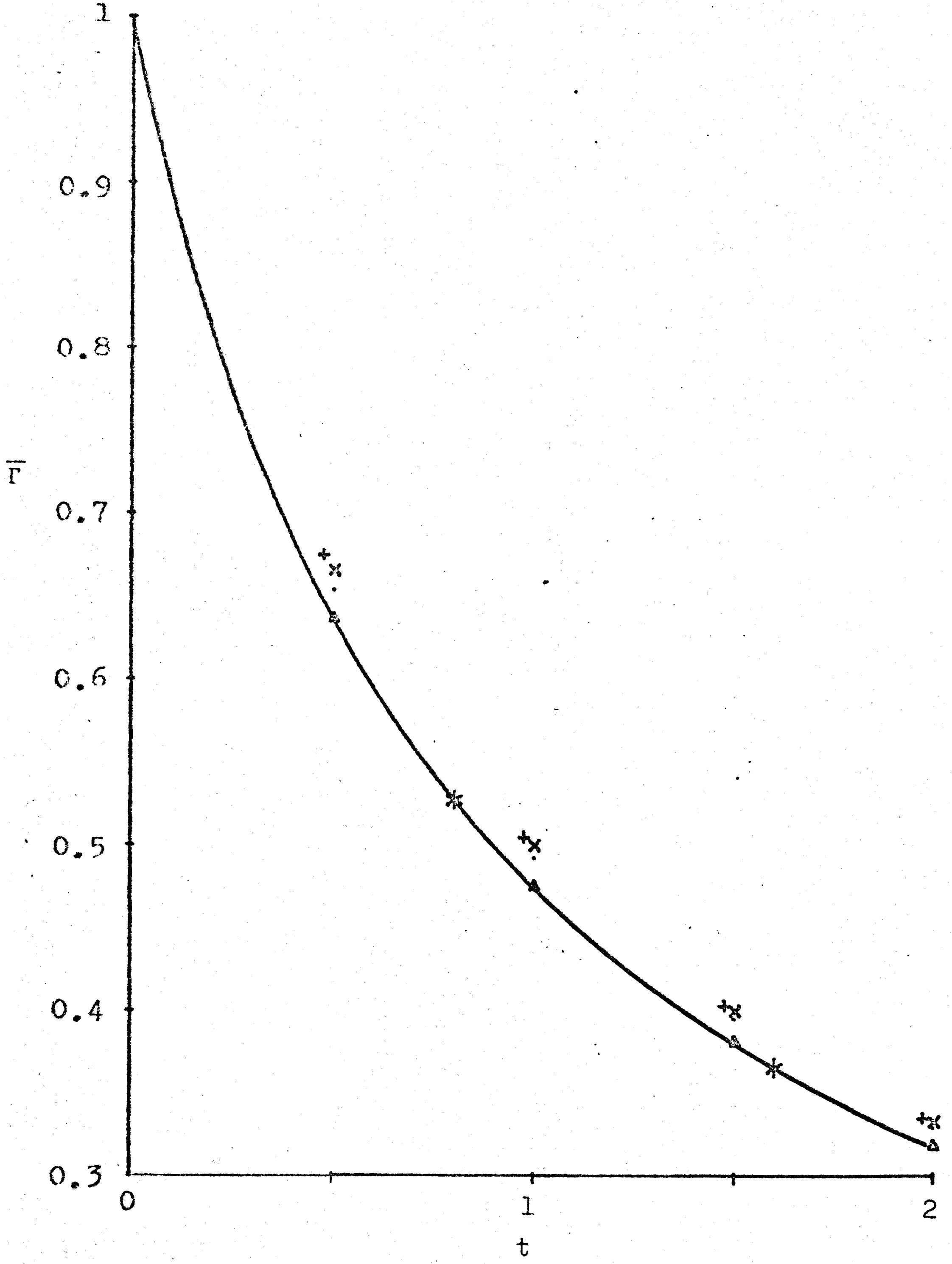

Fig. 2-1. Normalized mean concentration vs. dimensionless time for probability distribution Eq. (2.32)

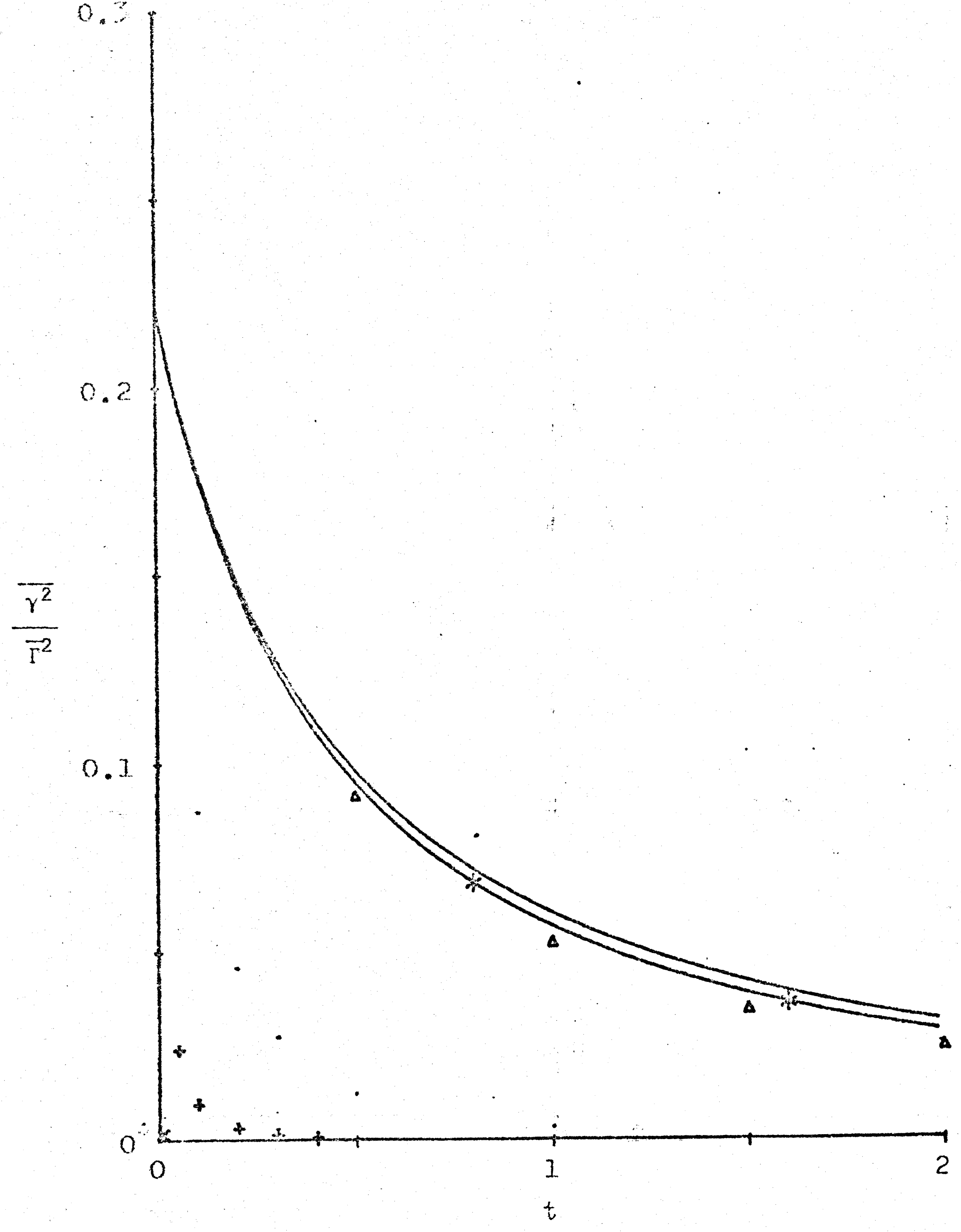

Fig. 2-2. Concentration relative intensity vs. dimensionless time for probability distribution Eq. (2.32)

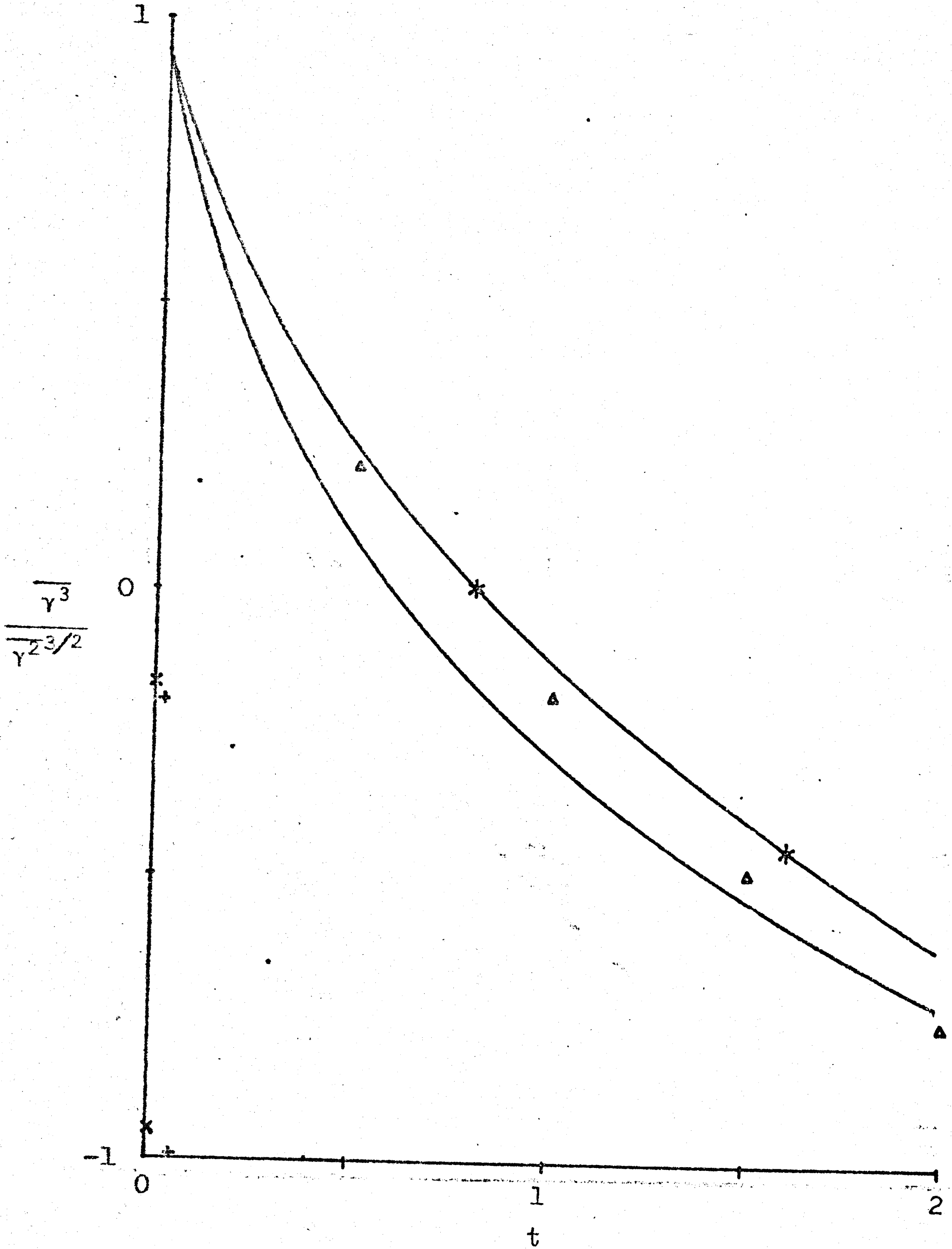

Fig. 2-3. Concentration skewness vs. dimensionless time for probability distribution Eq. (2.32)

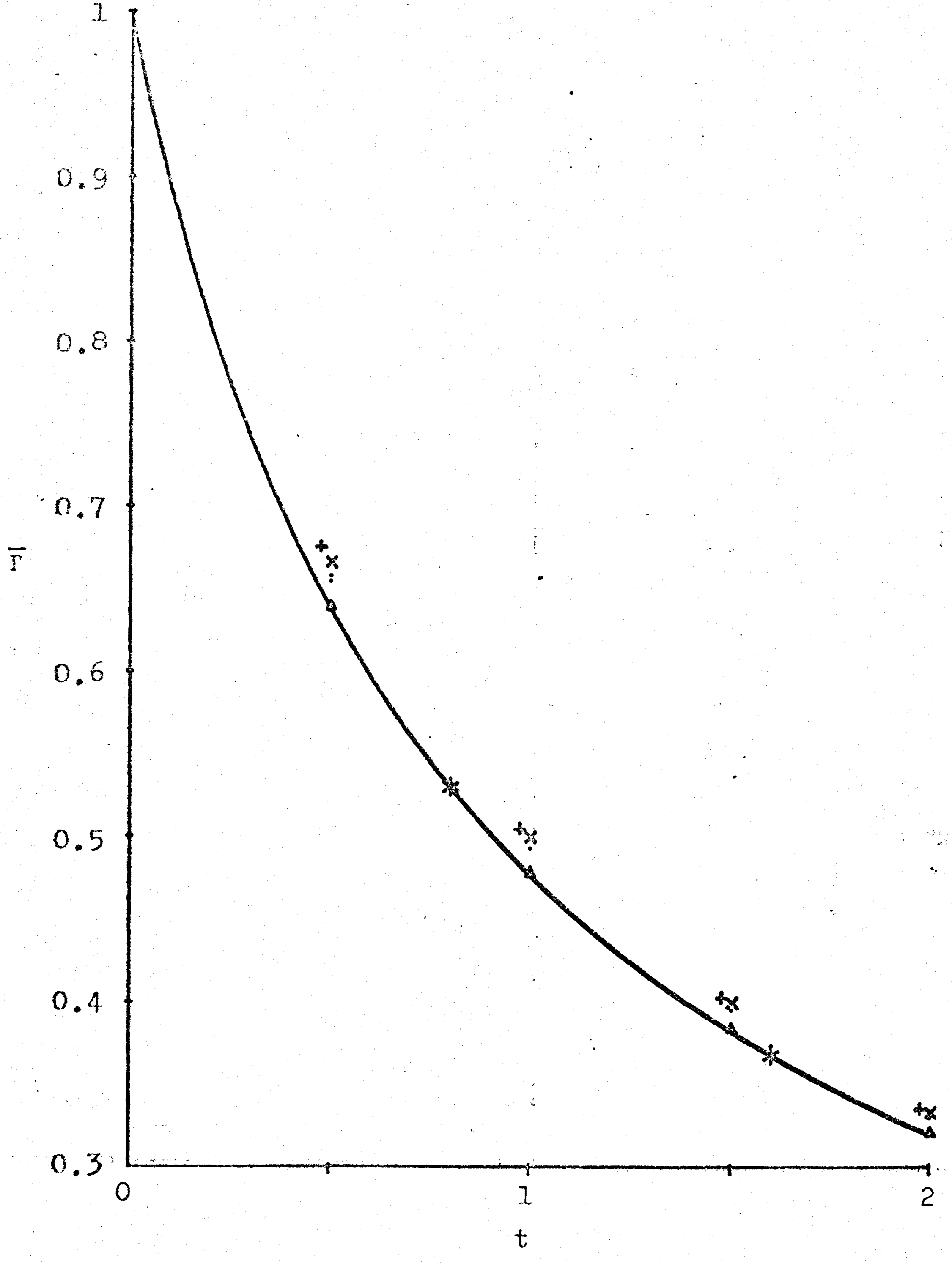

Fig. 3-1. Normalized mean concentration vs. dimensionless time for probability distribution Eq. (2.33), $\overline{\gamma^2}(0)=2/9$

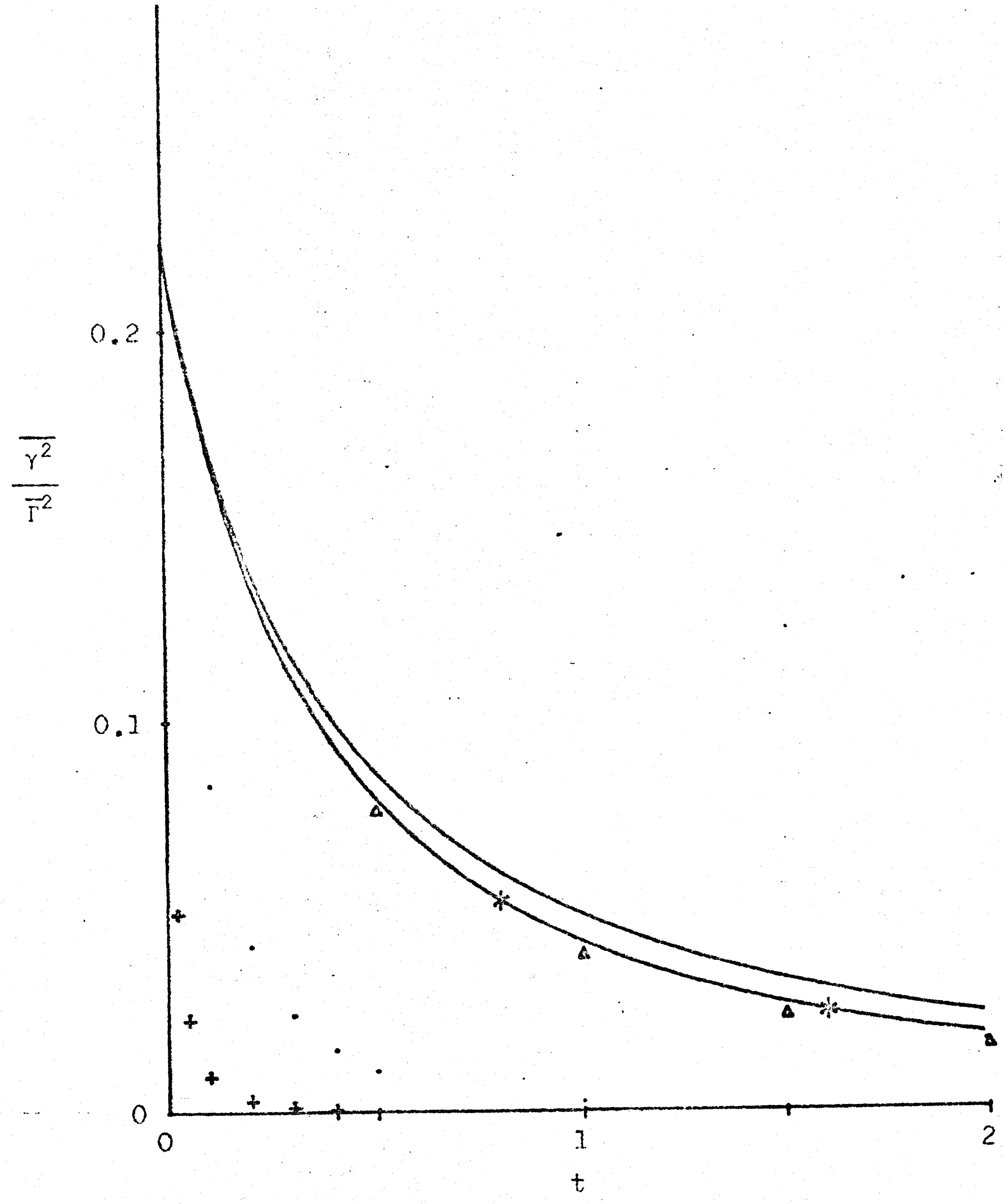

Fig. 3-2. Concentration relative intensity vs. dimensionless time for probability distribution Eq.(2.[illegible]), $\overline{\gamma^2}(0) = 2/9$

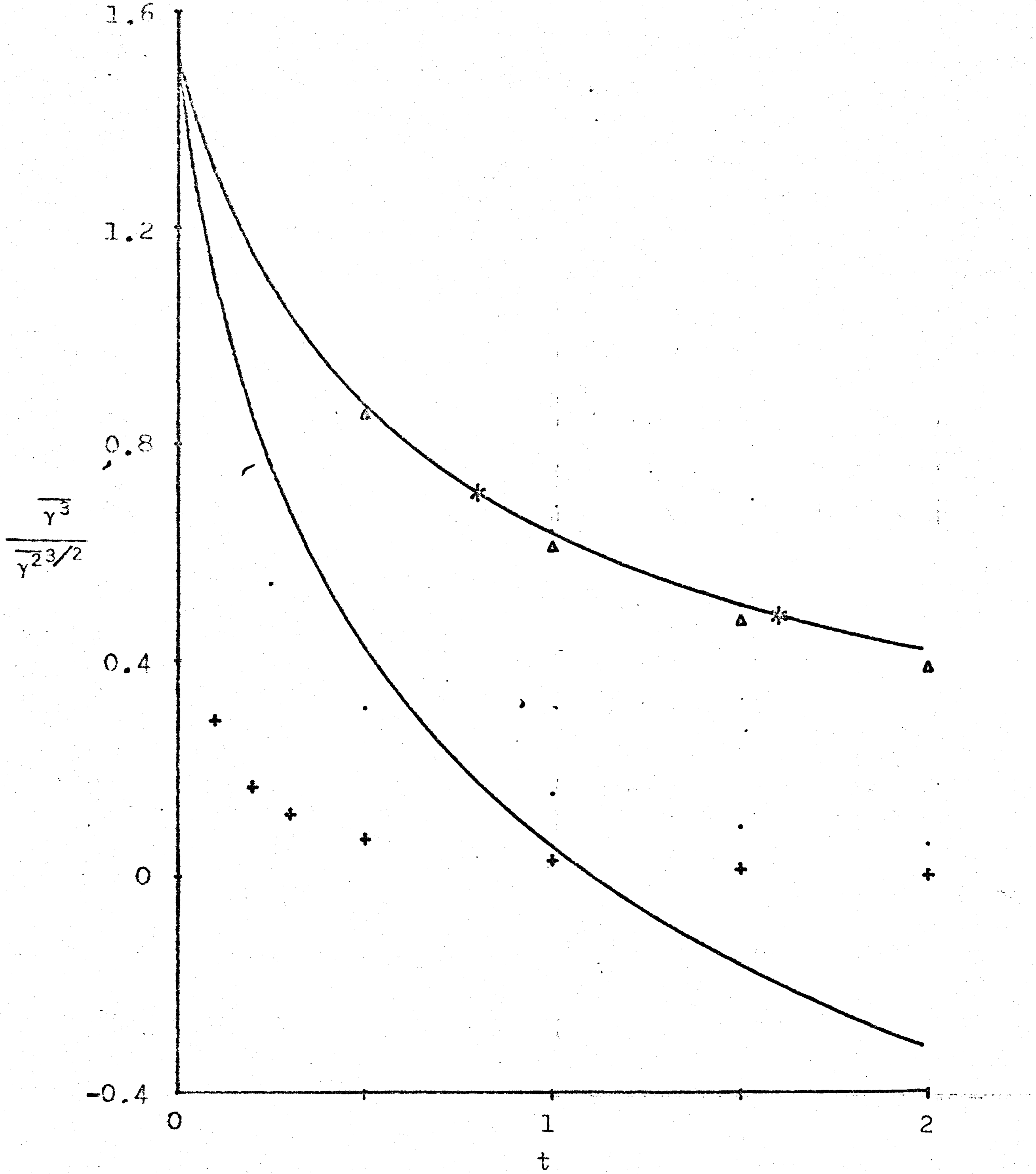

Fig. 3-3. Concentration skewness vs. dimensionless time for probability distribution Eq. (2.33), $\overline{\gamma^2}(0)=2/9$

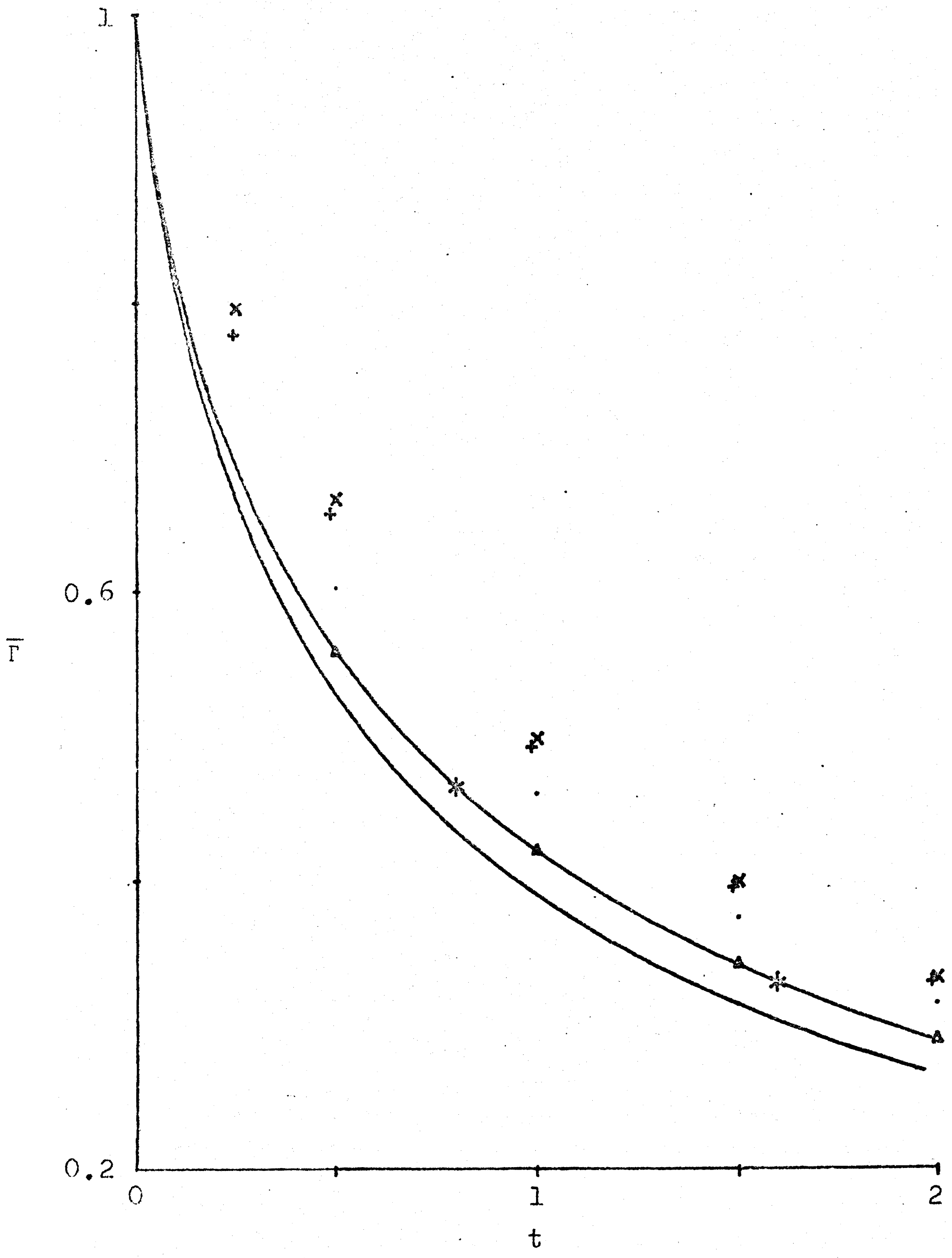

Fig. 4-1. Normalized mean concentration vs. dimensionless time for probability distribution Eq. (2.33). $\overline{\gamma^2}(0)=2$

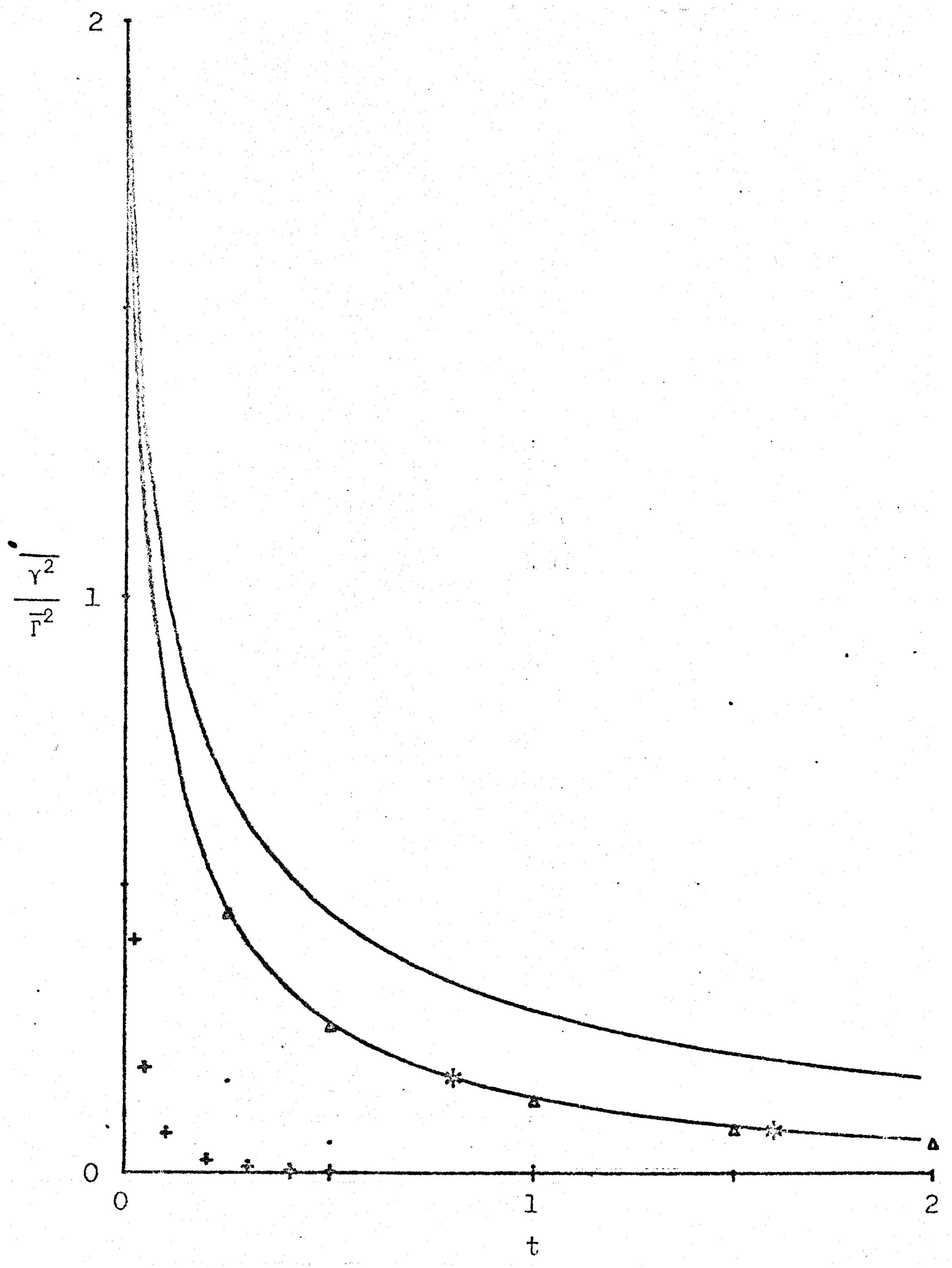

Fig. 4-2. Concentration relative intensity vs. dimensionless time for probability distribution Eq. (2.33), $\gamma^2(0)=2$

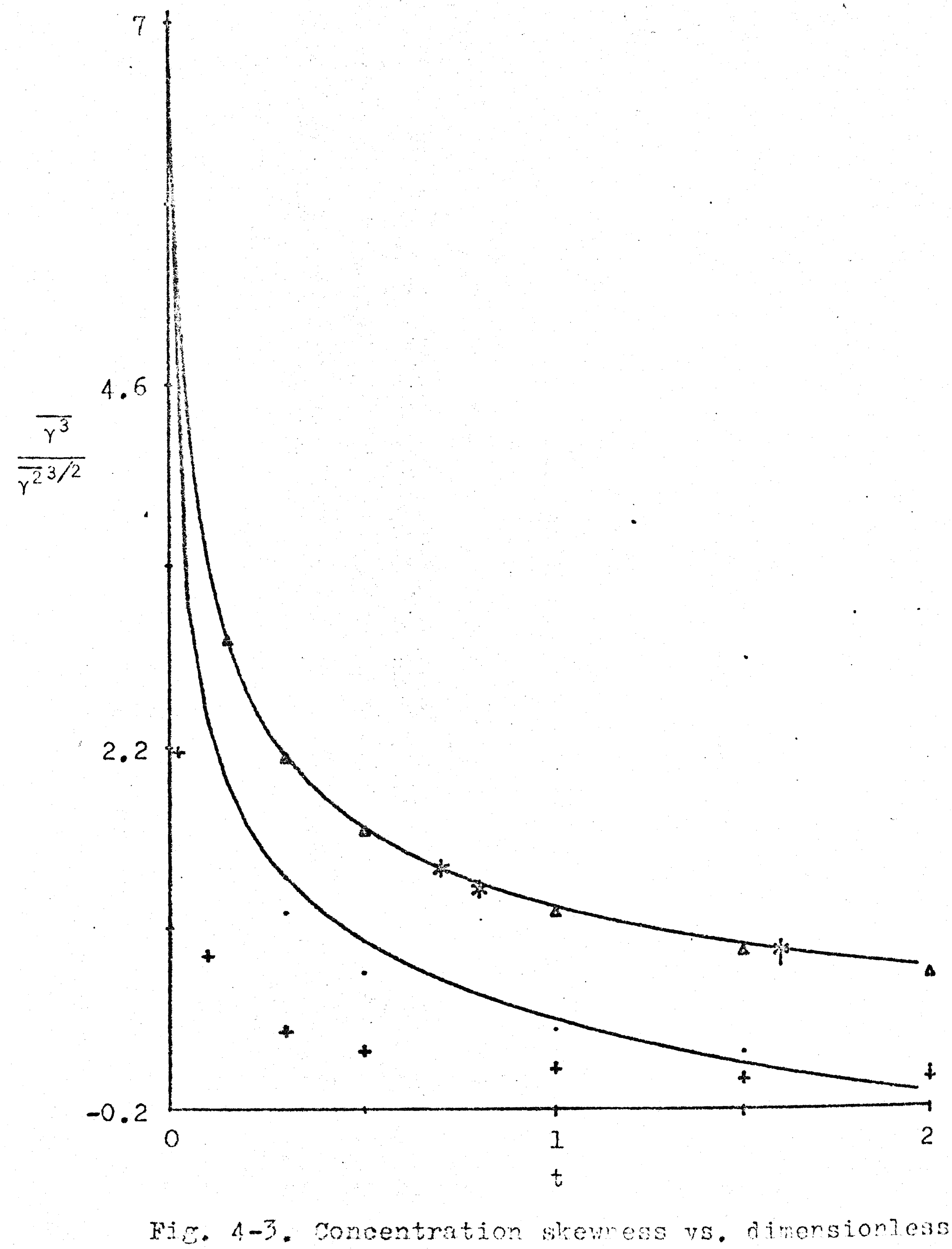

Fig. 4-3. Concentration skewness vs. dimensionless time for probability distribution Eq. (2.33), $\overline{\gamma^2}(0)=2$

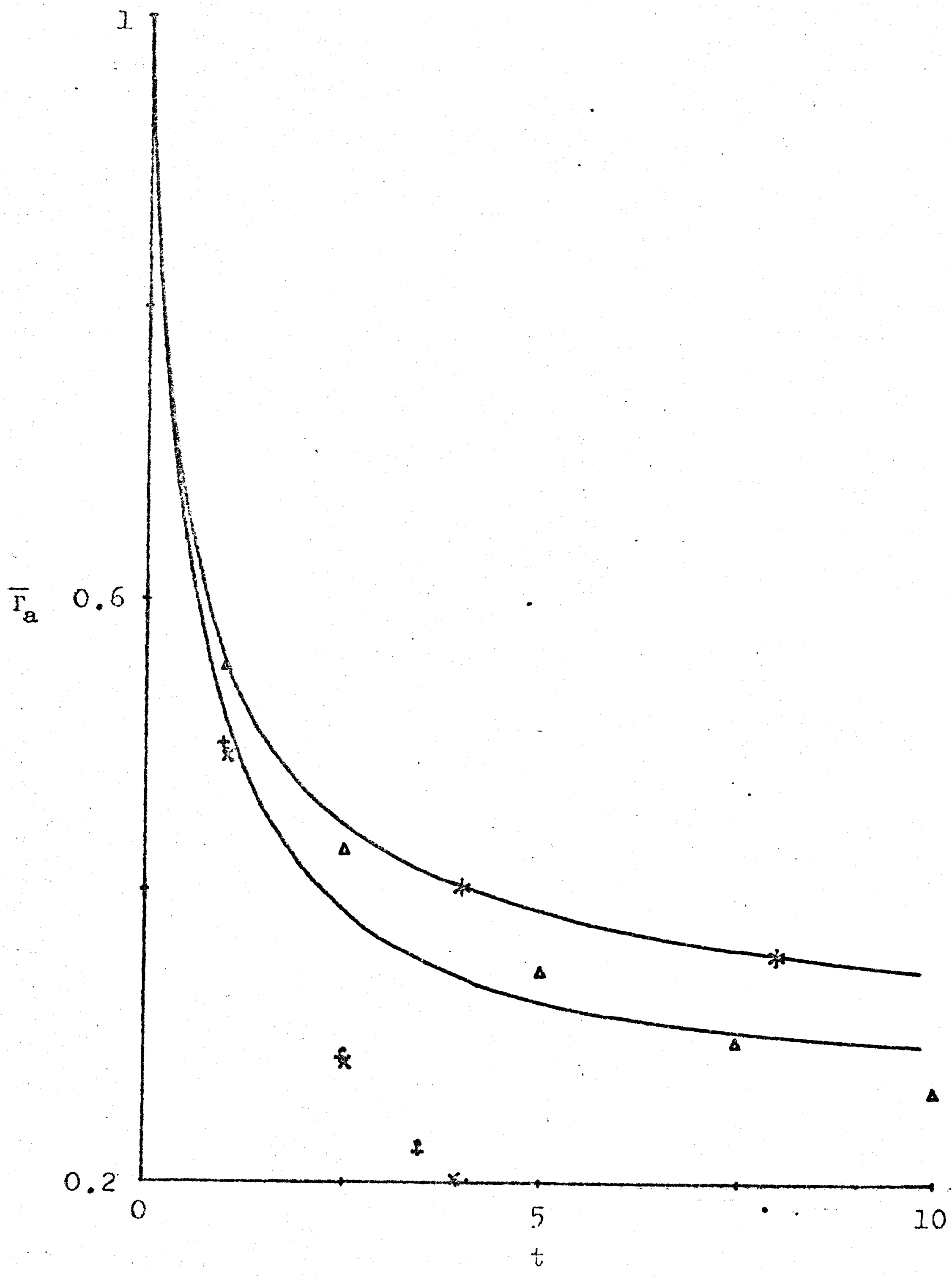

Fig. 5-1. Normalized mean concentration vs. dimensionless time, $w=0.75$, $\beta=1$, $\overline{\gamma_a^2}(0)=0.5$, $\overline{\gamma_b^2}(0)=2$, $\overline{\gamma_a\gamma_b}(0)=0.65$

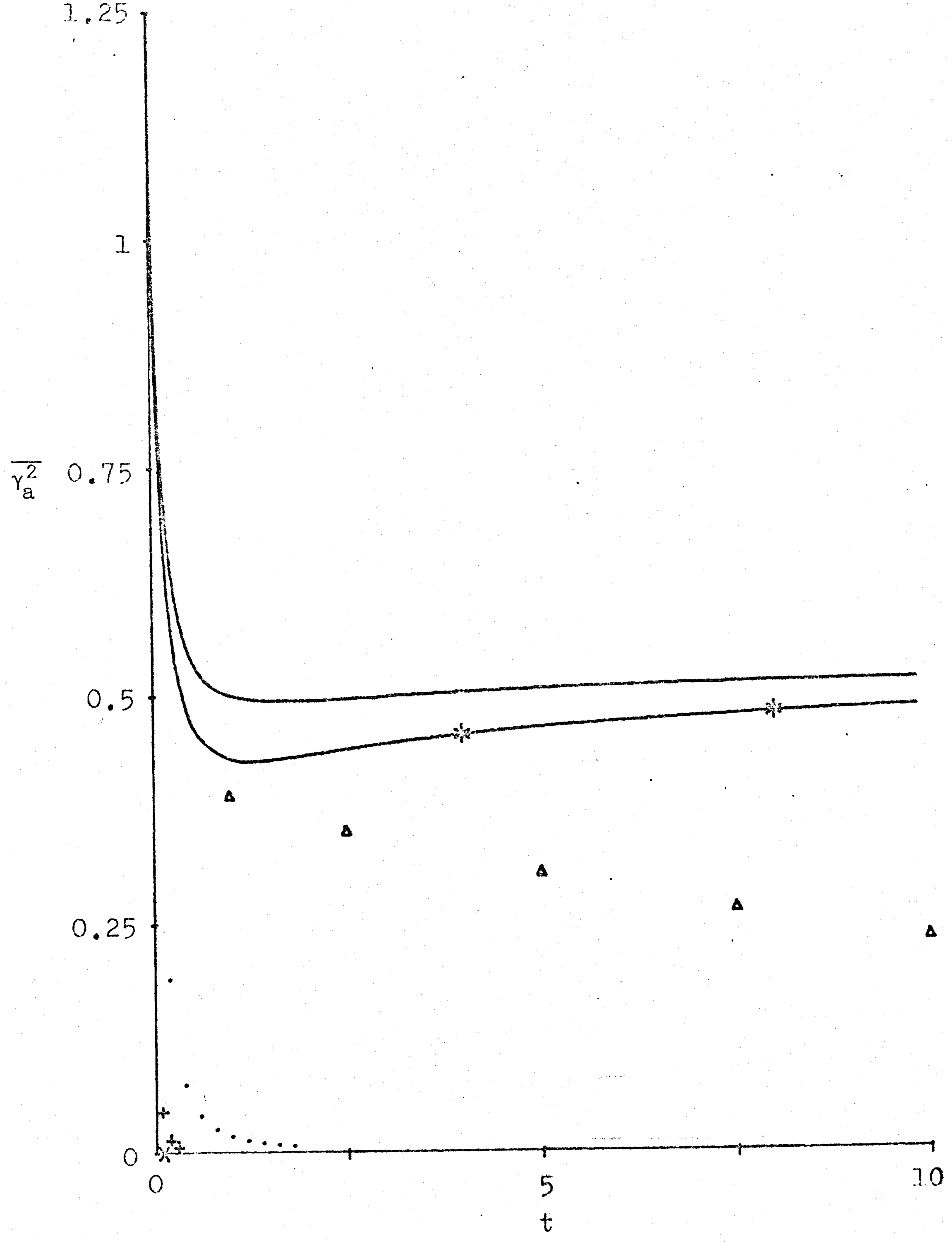

Fig. 5-2. Normalized concentration fluctuation vs. dimensionless time, k=0.75, β =1, $\overline{\gamma_a^2}(0)=0.5$, $\overline{\gamma_b^2}(0)=2$, $\overline{\gamma_a\gamma_b}(0)=0.65$

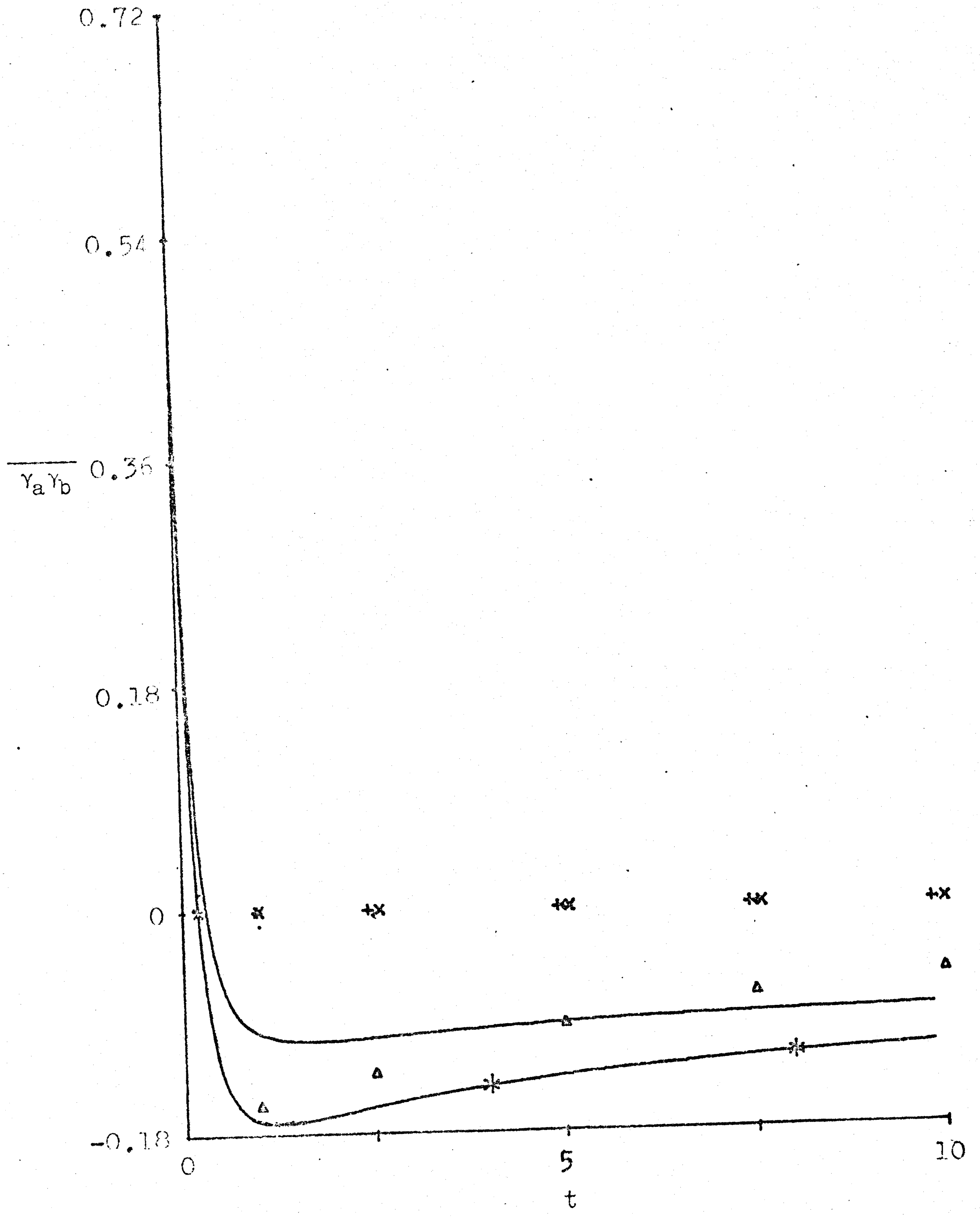

Fig. 5-7. Normalized concentration fluctuation cross moment vs. dimensionless time, w=0.75, $\beta=1$, $\overline{\gamma_a^2}(0)=0.5$, $\overline{\gamma_b^2}(0)=2$, $\overline{\gamma_a\gamma_b}(0)=0.65$

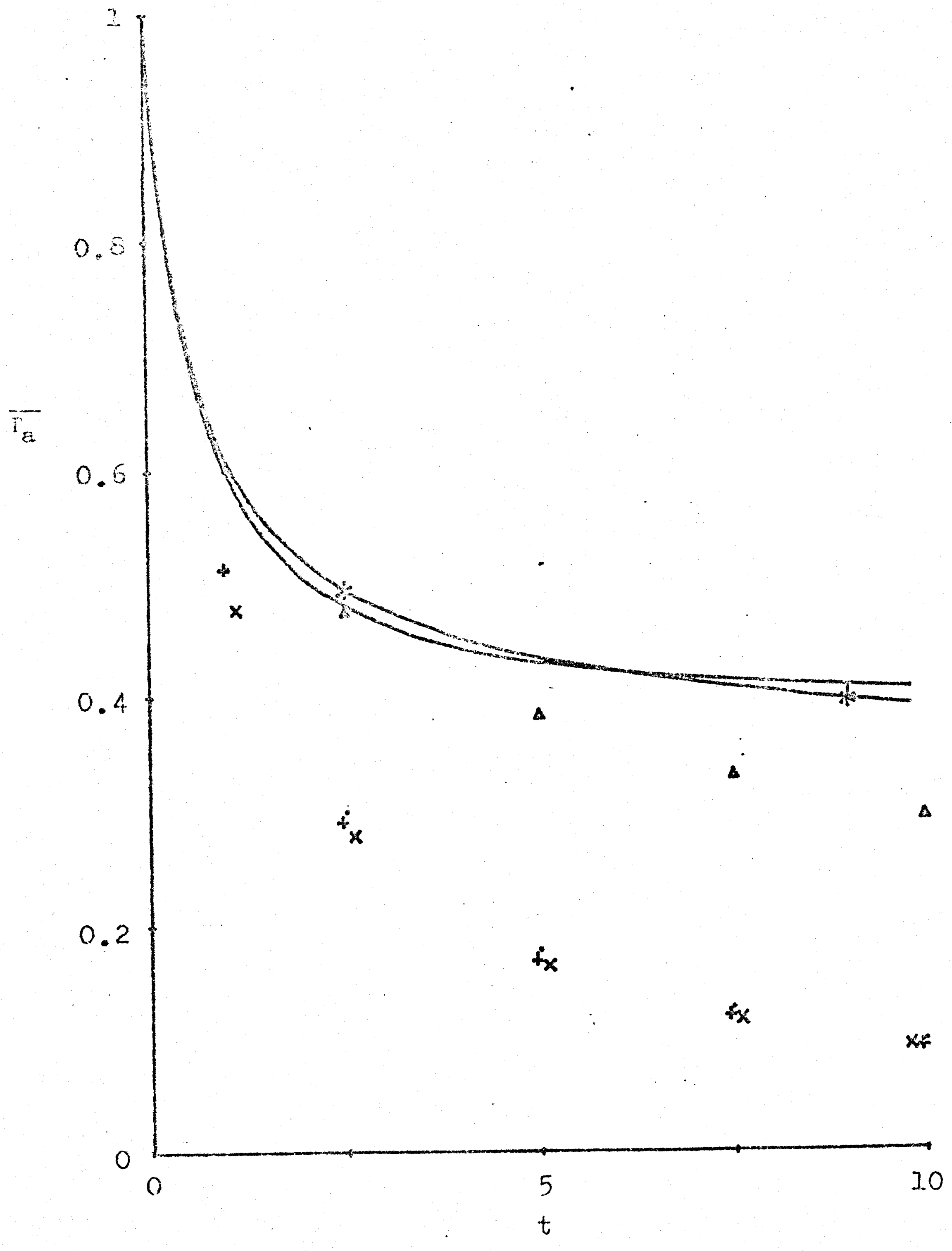

Fig. 6-1. Normalized mean concentration vs. dimensionless time, w=0.25, β=1, $\overline{\gamma_a^2}(0)=\overline{\gamma_b^2}(0)=1$, $\overline{\gamma_a\gamma_b}(0)=0.189$

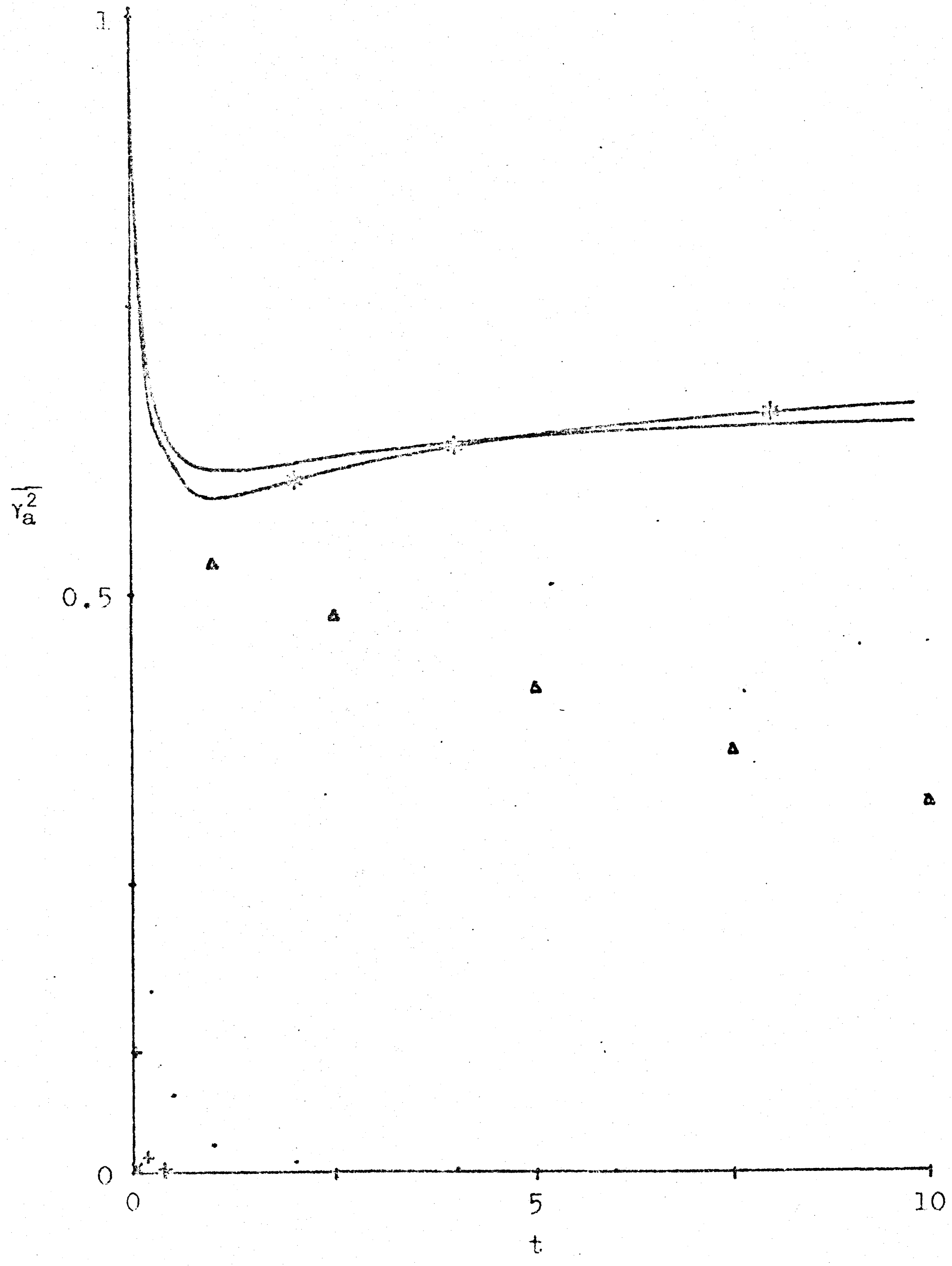

Fig. 6-2. Normalized concentration fluctuation vs. dimensionless time. w=0.25, β =1, $\overline{\gamma_a^2}(0)=\overline{\gamma_b^2}(0)=1$, $\overline{\gamma_a\gamma_b}(0)=0.189$

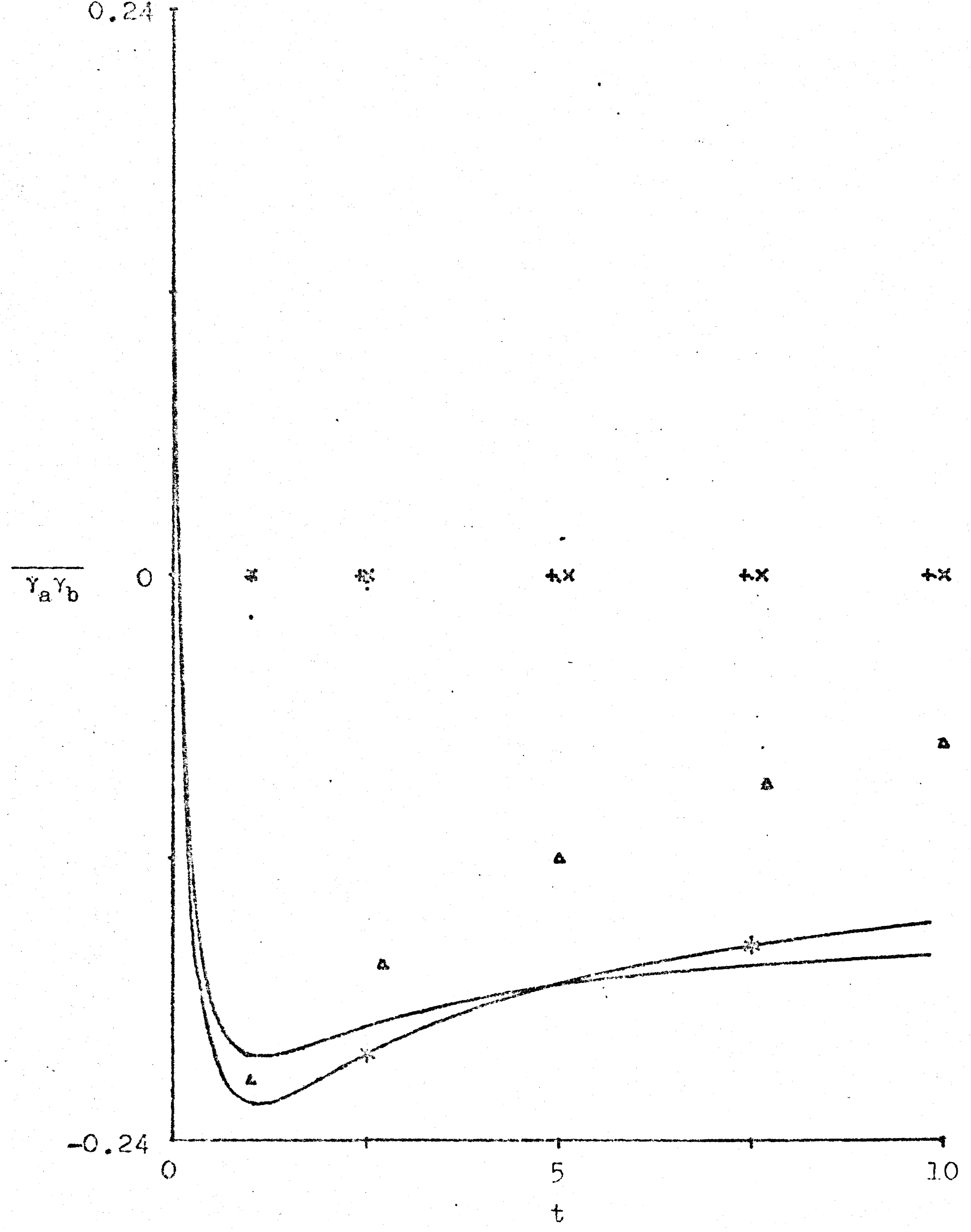

Fig. 6-3. Normalized concentration fluctuation cross moment vs. dimensionless time, w=0.25, $\beta=1$, $\overline{\gamma_a^2}(0)=\overline{\gamma_b^2}(0)=1$, $\overline{\gamma_a \gamma_b}(0)=0.189$

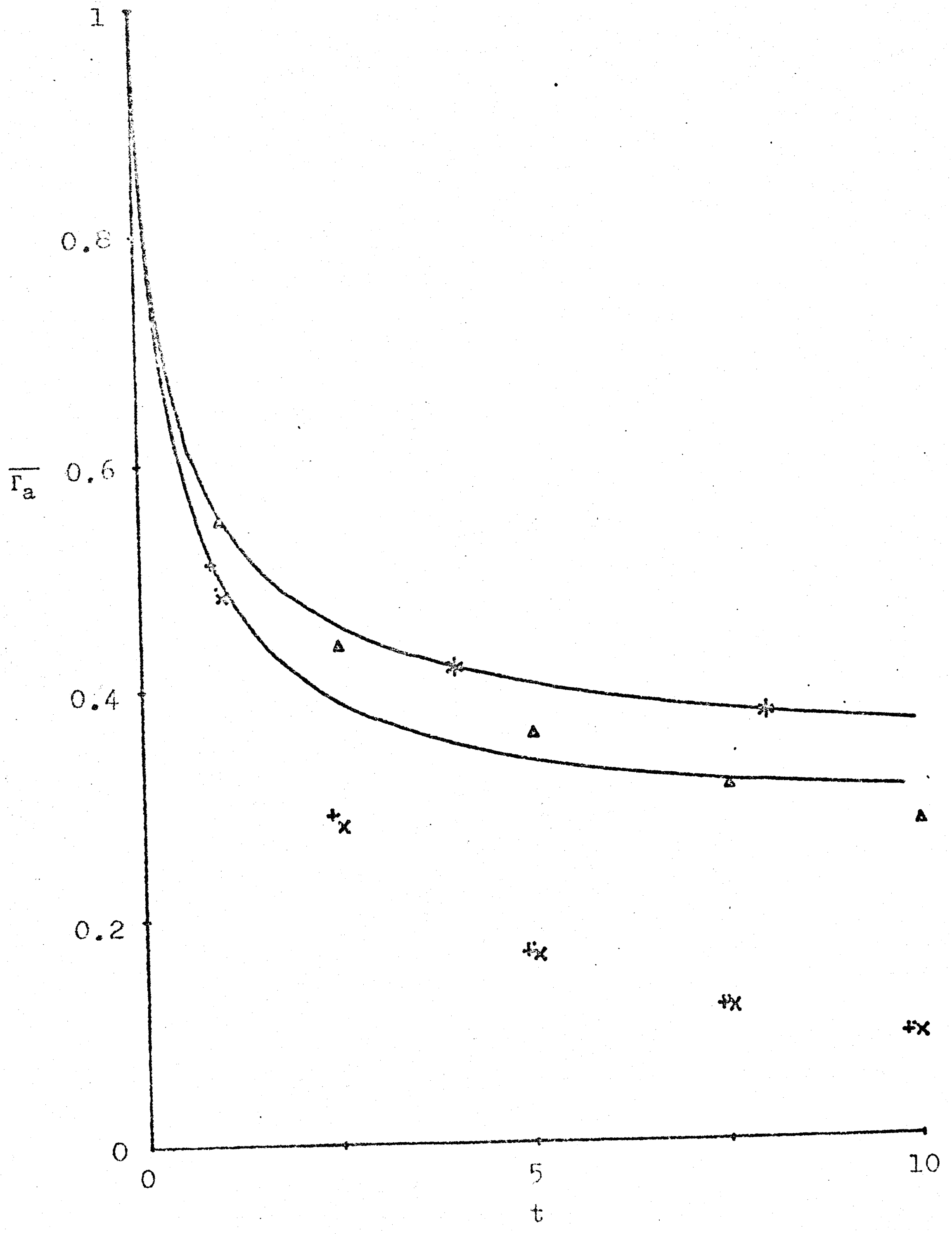

Fig. 7-1. Normalized mean concentration vs. dimensionless time, $w=0.75$, $\beta=1$, $\overline{\gamma_a^2}(0)$ $\overline{\gamma_b^2}(0)=2$, $\overline{\gamma_a\gamma_b}(0)=1.28$

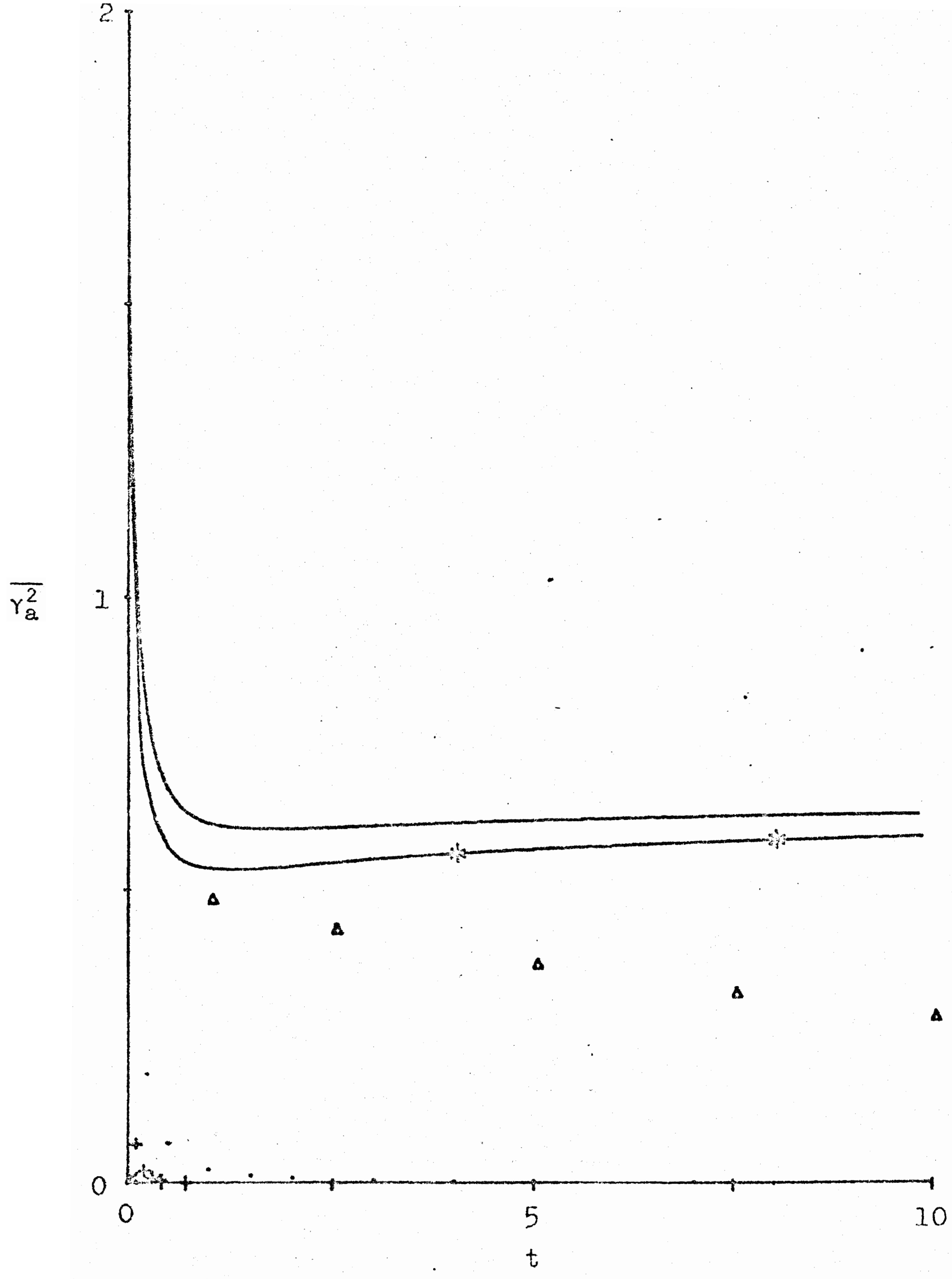

Fig. 7-2. Normalized concentration fluctuation vs. dimensionless time, w=0.75, β =1, $\overline{Y_a^2}(0)=\overline{Y_b^2}(0)=2$, $\overline{Y_a Y_b}(0)=1.28$

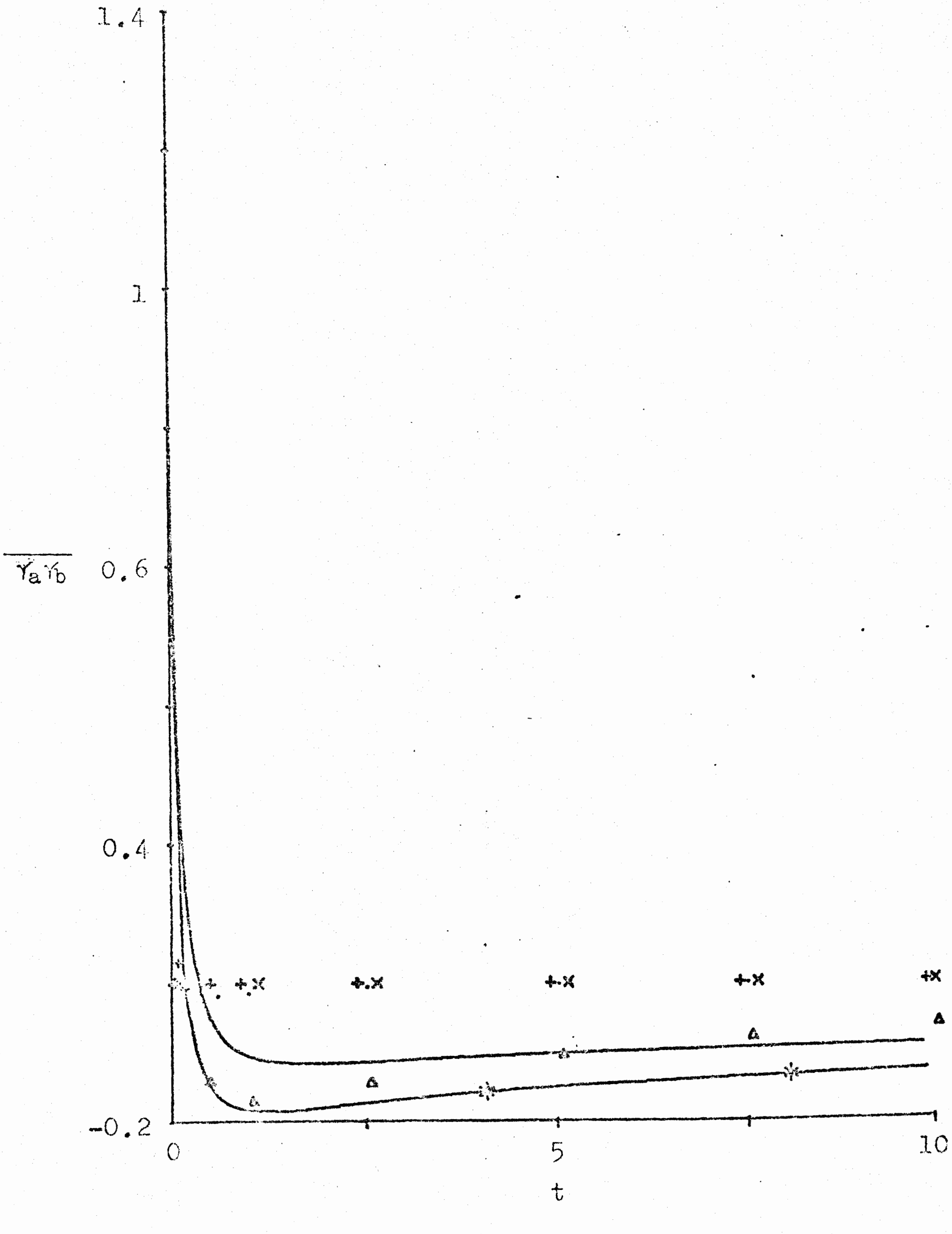

Fig. 7-3. Normalized concentration fluctuation cross moment vs. dimensionless time, w=0.75, β=1, $\overline{\gamma_a^2}(0)=\overline{\gamma_b^2}(0)=2$, $\overline{\gamma_a\gamma_b}$ [illegible] .28

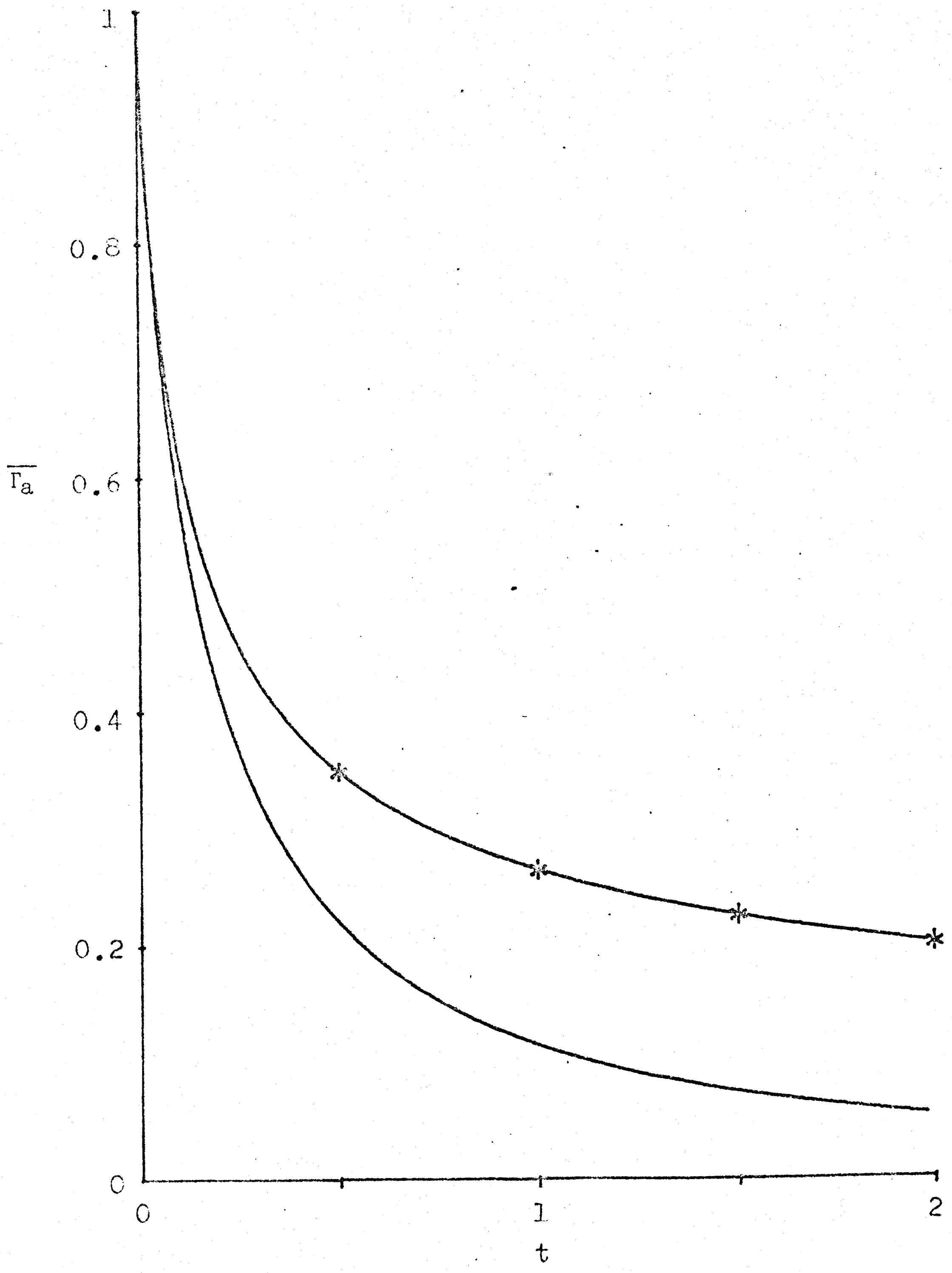

Fig. 8-1. Normalized mean concentration vs. dimensionless time, w=0.75, β =5, $\overline{\gamma_a^2}(0)$=0.5, $\overline{\gamma_b^2}(0)$=2, $\overline{\gamma_a \gamma_b}(0)$=0.65

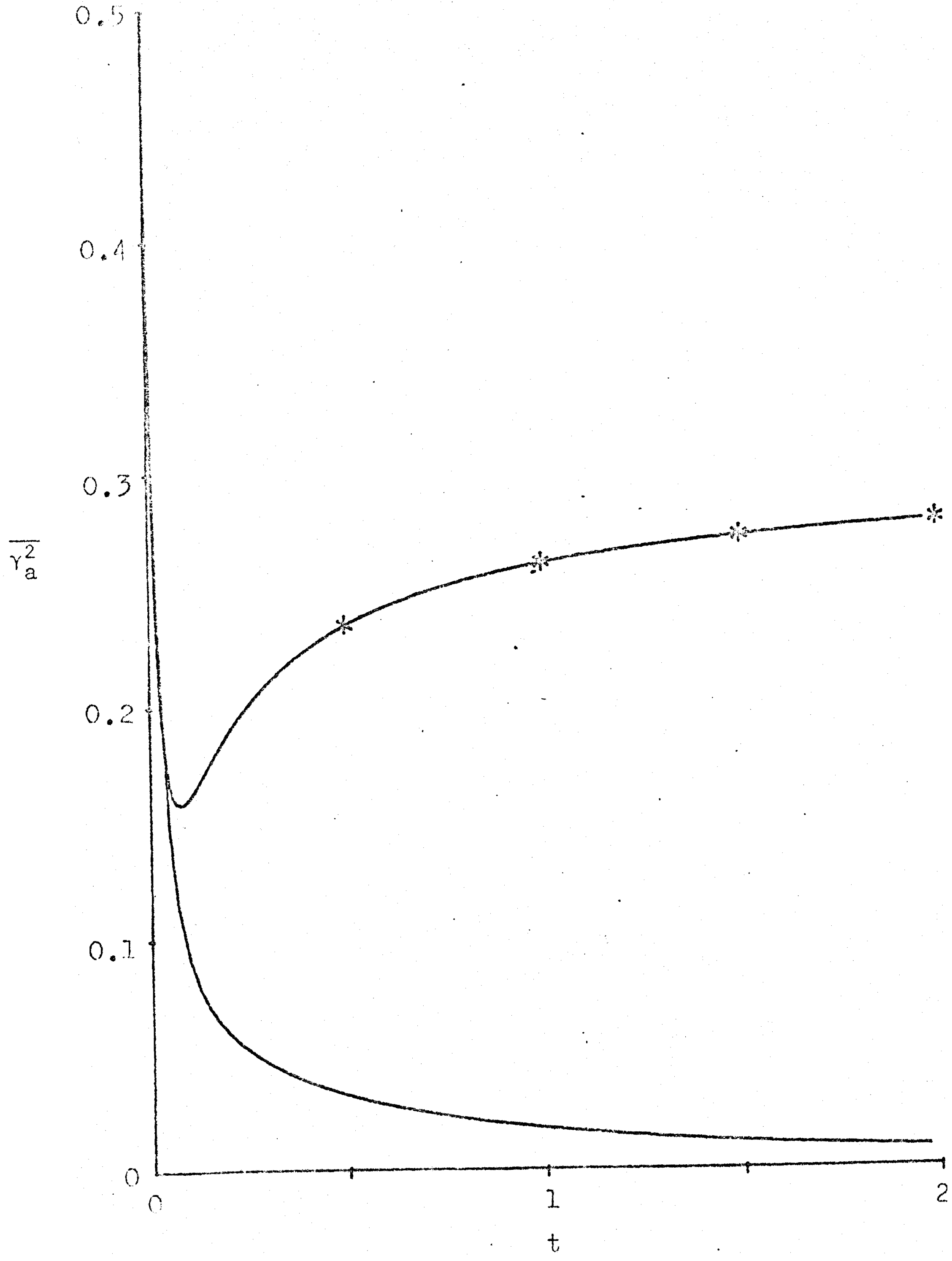

Fig. 8-2. Normalized concentration fluctuation vs. dimensionless time, w=0.75, β=5, $\overline{\gamma_a^2}(0)=0.5$, $\overline{\gamma_b^2}(0)=2$, $\overline{\gamma_a\gamma_b}(0)=0.65$

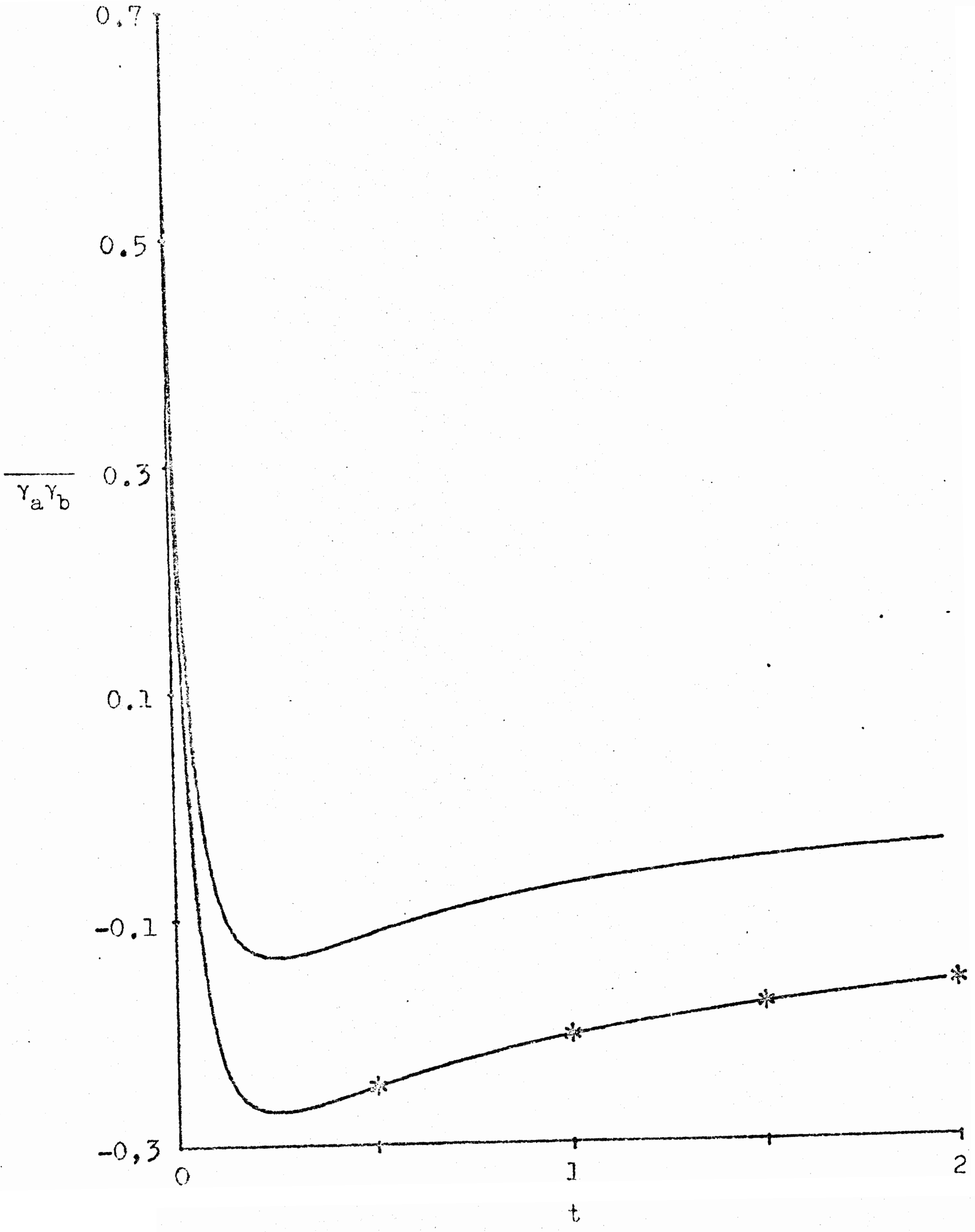

Fig. 8-3. Normalized concentration fluctuation cross moment vs. dimensionless time, w=0,75, $\beta=5$, $\overline{\gamma_a^2}(0)=0.5$, $\overline{\gamma_b^2}(0)=2$, $\overline{\gamma_a\gamma_b}(0)=0.65$

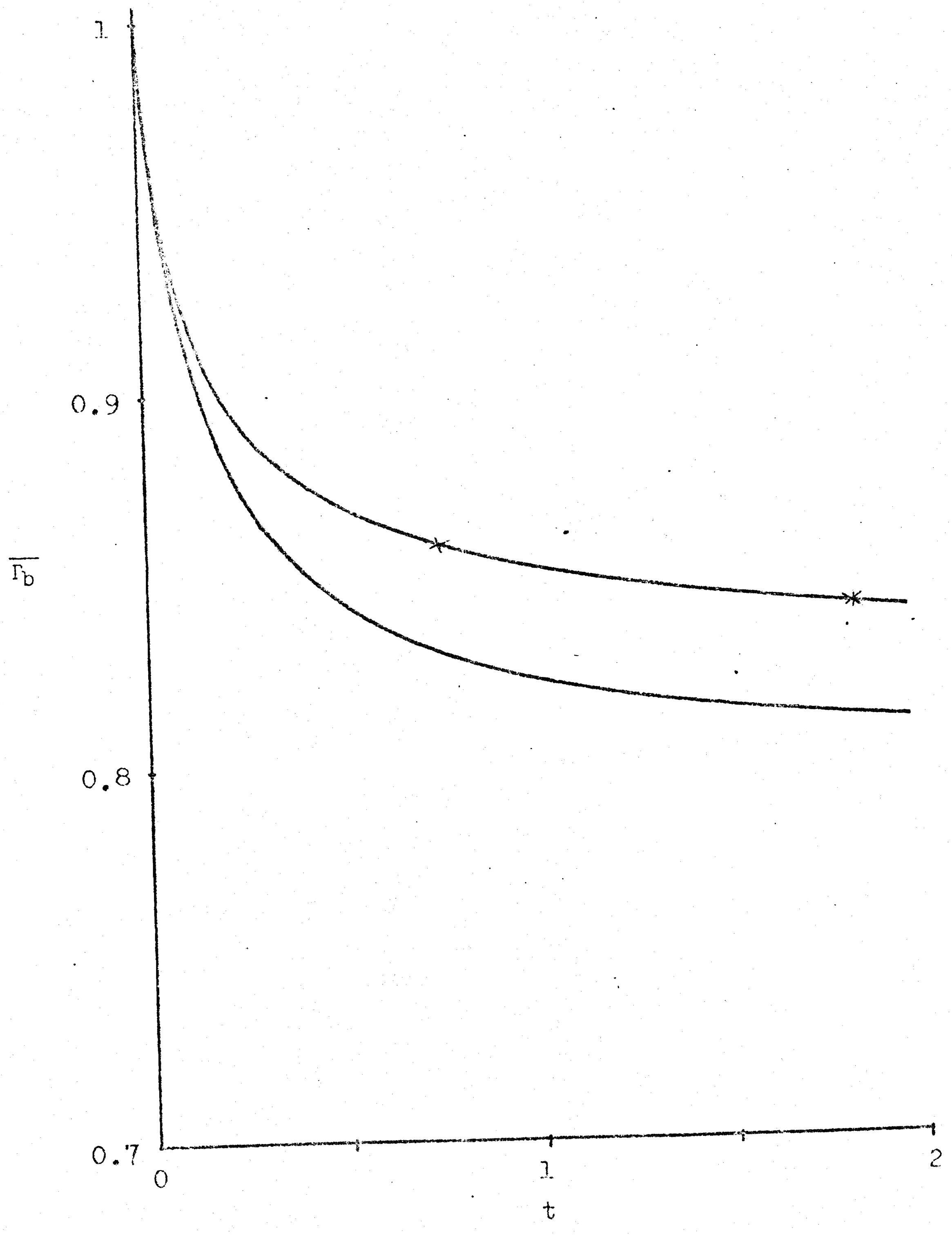

Fig. 8-4. Normalised mean concentration of over represented species vs. dimensionless time, w=0.75, β=5, $\overline{\gamma_1}(0)=0.5$, $\overline{\gamma_2}(0)=2$, $\overline{\gamma_1\gamma_2}(0)=0.65$

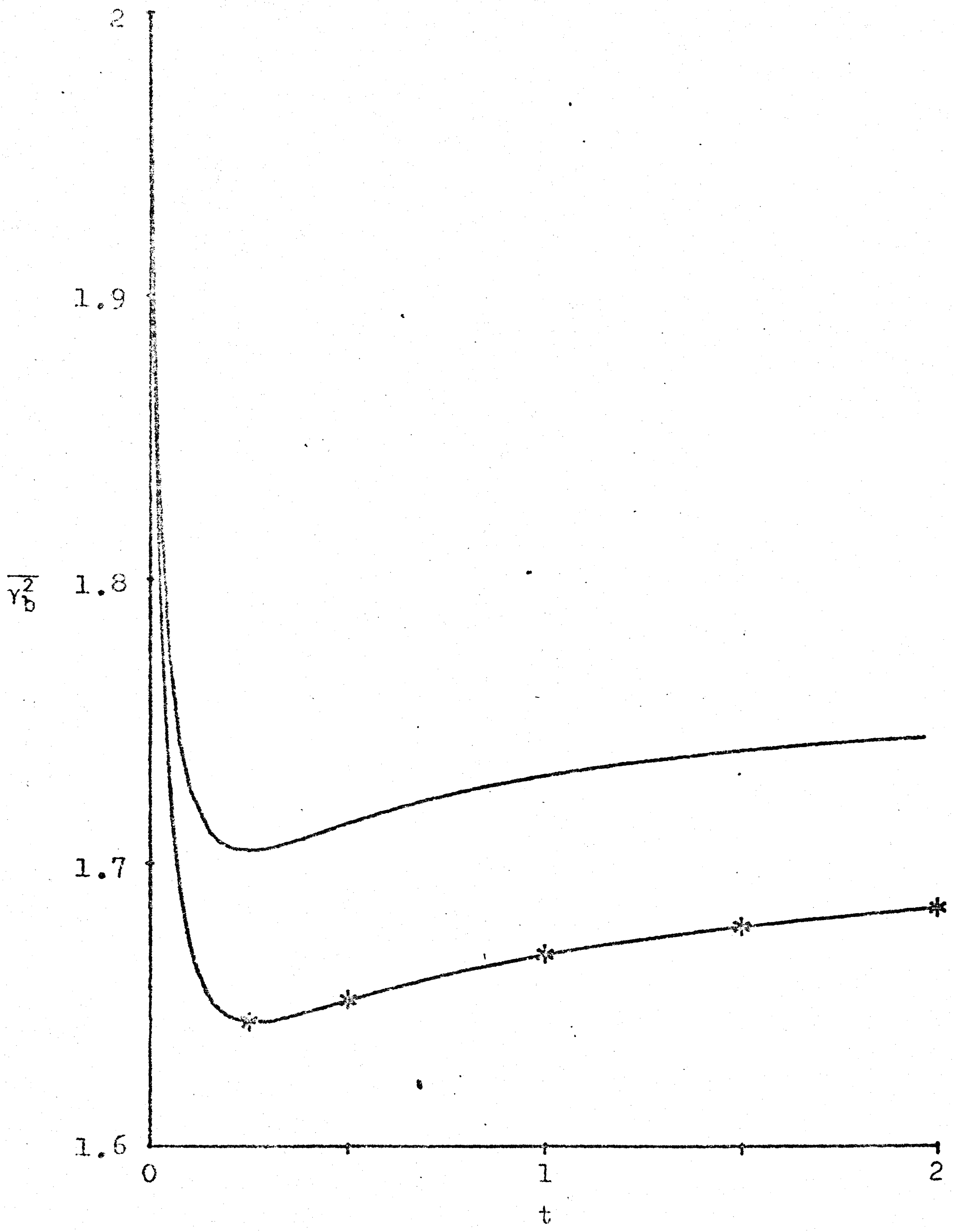

Fig. 8-5. Normalized concentration fluctuation of over represented species vs. dimensionless time, $\beta=5$, $\overline{\gamma_a^2}(0)=0.5$, $\overline{\gamma_b^2}(0)=2$, $\overline{\gamma_a\gamma_b}(0)=0.65$, w=0.75

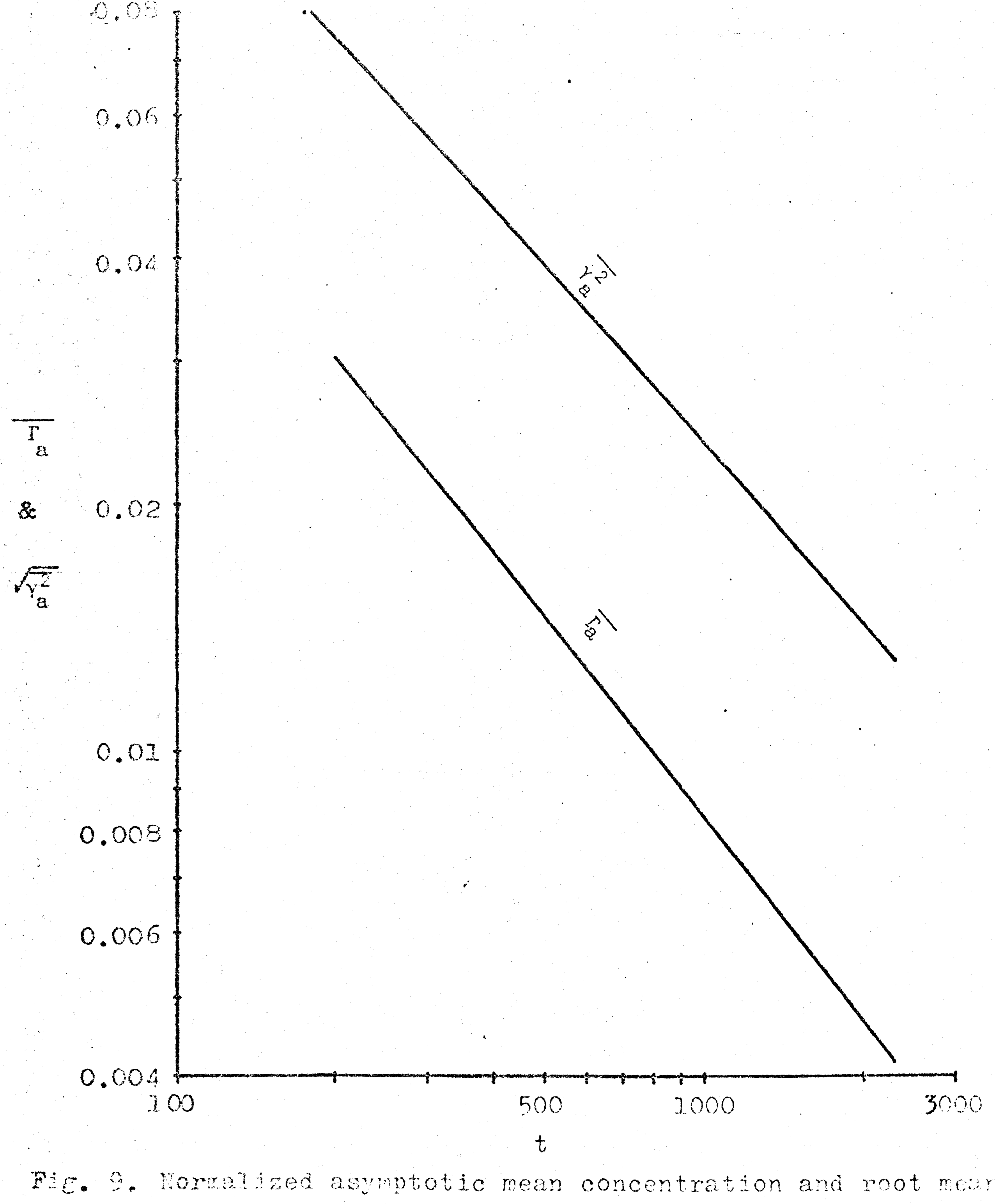

Fig. 9. Normalized asymptotic mean concentration and root mean square concentration fluctuation vs. dimensionless time, $w=0.75$, $\beta=1$, $\alpha=0.01$, $\overline{\gamma_a^2}(0)=\overline{\gamma_b^2}(0)=2$, $\overline{\gamma_a\gamma_b}(0)=1.28$

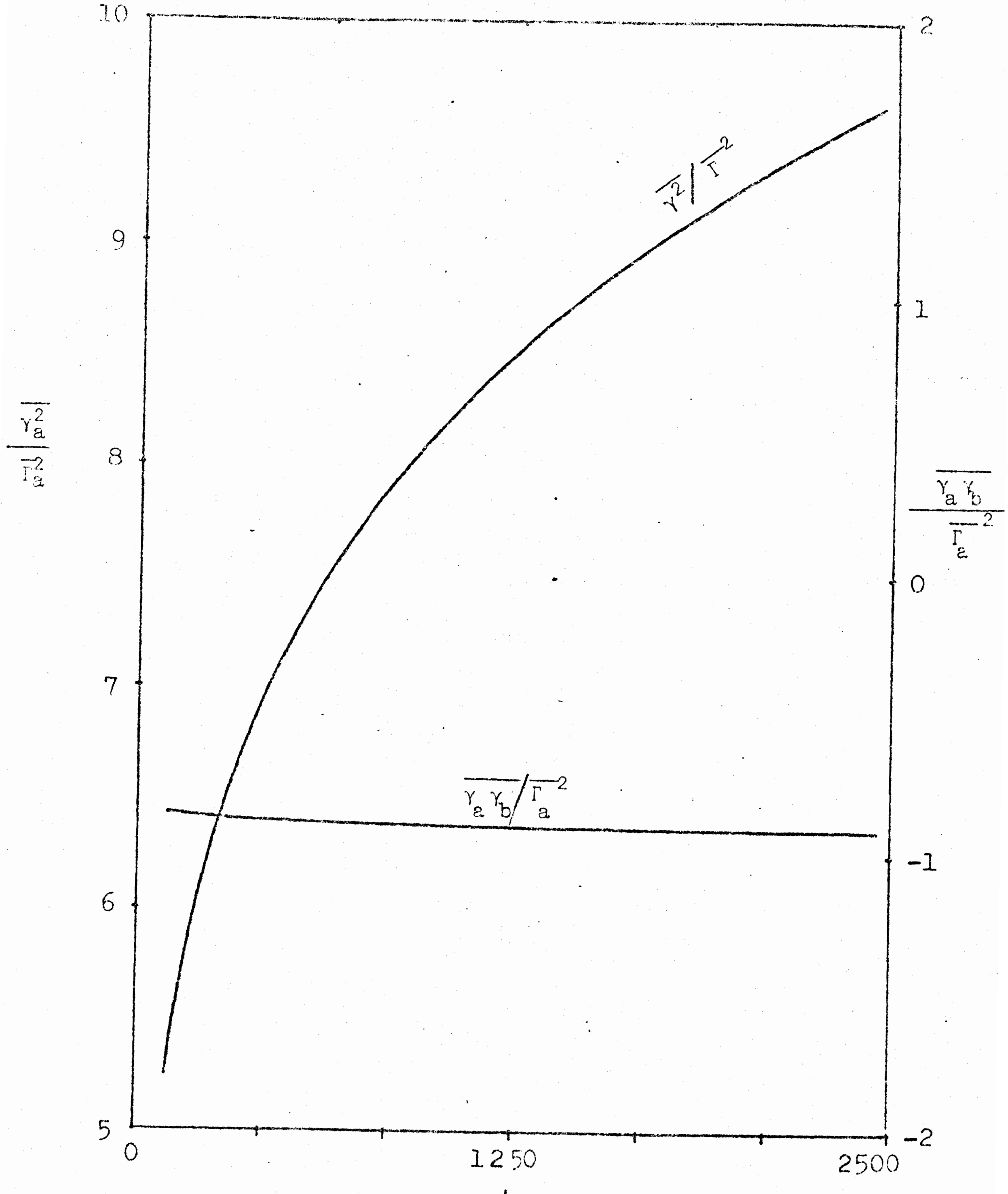

Fig. 10. Asymptotic concentration relative intensity and concentration fluctuation cross moment relative to mean vs. dimensionless time, $w=0.75$, $\beta=1$, $\alpha=0.01$, $\overline{\gamma_a^2}(0)=\overline{\gamma_b^2}(0)=2$, $\overline{\gamma_a \gamma_b}(0)=1.25$

Table 1. Normalized mean concentration, concentration relative intensity and concentration skewness of one species second-order chemical reaction at a particular dimensionless time, $\overline{\Gamma}(0)=1$

(1). For probability distribution $P(y)=60y^2(1+y)^{-7}$ and $t=2$, $\overline{\gamma^2}(0)=1$

	EXACT SOLUTION	CLOSURE APPROXIMATE SOLUTION				
α	0	0	.01	1	10	100
$\overline{\Gamma}$	.2896	.3100	.3106	.3238	.3310	.3330
COMPLETENESS ξ	71.04	69.00	68.94	67.62	66.90	66.70
$\overline{\gamma^2}/\overline{\Gamma}^2$	.0902	.0151	.0129	.0005		
$\overline{\gamma^3}/\overline{\gamma^2}^{3/2}$	-.2973	4.562	4.857	22.89		

(2). For probability distribution $P(y)=4.5(3.5!)^{-1}(4.5y)^{3.5}e^{-4.5y}$ and $t=2$, $\overline{\gamma^2}(0)=2/9$

	EXACT SOLUTION	CLOSURE APPROXIMATE SOLUTION				
α	0	0	.01	1	10	100
$\overline{\Gamma}$	.3171	.3176	.3185	.3298	.3327	.3333
COMPLETENESS ξ	68.30	68.24	68.15	67.02	66.73	66.67
$\overline{\gamma^2}/\overline{\Gamma}^2$	.0313	.0286	.0243	.0006		
$\overline{\gamma^3}/\overline{\gamma^2}^{3/2}$	-.7226	-.6243	-.7538	-7.273		

Table 1. (continued)

(3). For probability distribution

$$F(y)=\frac{1}{\sqrt{2\pi}\,\sigma y}\,\mathrm{EXP}\left\{-\frac{(\ln y-\mu)^2}{2\sigma^2}\right\}\quad\text{and}\quad t=2$$

	$\overline{\gamma^2}(0)$	EXACT SOLUTION	CLOSURE APPROXIMATE SOLUTION				
α		0	0	.01	1	10	100
$\overline{\Gamma}$	2/9	.3189	.3201	.3208	.3300	.3328	.3333
	1/2	.3052	.3096	.3106	.3265	.3320	.3271
	1	.2874	.2984	.2997	.3214	.3308	.3330
	3/2	.2745	.2920	.2933	.3176	.3297	.3332
	2	.2646	.2878	.2891	.3147	.3287	.3328
COMPLETENESS, %	2/9	68.11	67.99	67.92	67.00	66.73	66.67
	1/2	69.48	69.04	68.94	67.35	66.80	67.29
	1	71.26	70.16	70.03	67.86	66.92	66.70
	3/2	72.55	70.80	70.67	68.24	67.03	66.68
	2	73.54	71.22	71.09	68.53	67.13	66.72
$\overline{\gamma^2}/\overline{\Gamma}^2$	2/9	.0243	.0190	.0161	.0004		
	1/2	.0524	.0331	.0281	.0005		
	1	.0962	.0465	.0399	.0011		
	3/2	.1330	.0533	.0463	.0016		
	2	.1647	.0576	.0496	.0040		
$\overline{\gamma^3}/\overline{\gamma^2}^{3/2}$	2/9	-.3181	.4161	.3823	.0578		
	1/2	-.3161	.5516	.5073	.0668		
	1	-.2430	.6549	.6076	.1007		
	3/2	-.1672	.7087	.6556	.1189		
	2	[illegible]	[illegible]	.6792	[illegible]		

Table 2. Normalized mean concentration and completeness of reaction of two species second-order chemical reaction at a dimensionless time, t=10, and $\beta=1$

	EXACT SOLUTION		CI ω APPROXIMATE SOLUTION													
α	0		0		.01		1		3		10		100		$\overline{\gamma_a^2(0)}$	$\overline{\gamma_b^2(0)}$
w	0	.75	0	.75	0	.75	0	.75	0	.75	0	.75	0	.75		
$\overline{\Gamma}_a$	.343	.203	.328	.206	.252	.169	.095	.092	.0918	.0910	.0911	.0909	.0909	.0909	.5	.5
COMPLETE-NESS, %	65.3	79.7	67.1	79.4	74.8	83.1	90.5	90.8	90.82	90.90	90.89	90.91	90.91	90.91		
$\overline{\Gamma}_a$	.411	.239	.383	.253	.286	.202	.097	.093	.0922	.0911	.0911	.0909	.0909	.0909	.5	1
COMPLETE-NESS, %	58.9	76.1	61.7	74.7	71.4	79.8	90.3	90.7	90.78	90.89	90.89	90.91	90.91	90.91		
$\overline{\Gamma}_a$	.471	.294	.466	.344	.338	.262	.100	.095	.0930	.0916	.0913	.0909	.0909	.0909	.5	2
COMPLETE-NESS, %	52.9	70.6	53.4	65.6	66.2	73.8	89.9	90.5	90.70	90.84	90.87	90.91	90.91	90.91		
$\overline{\Gamma}_a$	.429	.252	.426	.271	.314	.214	.098	.093	.0926	.0911	.0912	.0909	.0909	.0909	1	1
COMPLETE-NESS, %	57.1	74.8	57.4	72.9	68.6	78.6	90.2	90.7	90.74	90.89	90.88	90.91	90.91	90.91		
$\overline{\Gamma}_a$	.505	.291	.494	.336	.356	.258	.102	.095	.0934	.0915	.0914	.0909	.0909	.0909	1	2
COMPLETE-NESS, %	49.5	70.9	50.6	66.4	64.4	74.2	89.8	90.5	90.66	90.85	90.86	90.91	90.91	90.91		
$\overline{\Gamma}_a$	.524	.306	.541	.364	.387	.275	.105	.096	.0942	.0916	.0915	.0909	.0909	.0909	2	3
COMPLETE-NESS, %	47.6	69.4	45.9	63.6	61.3	72.5	89 5	90.4	90.58	90.84	90.85	90.91	90.91	90.91		