excite metal particles.

However, it can provide an efficient method for the direct analysis of conducting samples and the moderate power system performs better than the low power. A simple calculation reveals that dried solid aerosol introduction is one order of magnitude more sensitive than the aqueous sample introduction.

References

1. Codeo, A. G.; Lopez, M. T. D.; Seco, J. L. J.; Cobo, I. *J. Anal. At. Spectrom.* **1992**, *7*, 11.
2. Ono, A.; Saeki, A.; Chiba, K. *Appl. Spectrosc.* **1987**, *41*, 970.
3. Marks, J. Y.; Fornwalt, D. E.; Yungk, D. E. *Spectrochim. Acta. Part B* **1983**, *83*, 107.
4. Human, H. G. C.; Scott, R. H.; Oakes, A. R.; West, C. D. *Analyst* **1976**, *101*, 265.
5. Aziz, A.; Broekaert, J. A. C.; Laqua, K.; Leis, F. *Spectrochim. Acta. Part B* **1984**, *39*, 1091.
6. Marks, J. Y.; Fornwalt, D. E.; Yungk, R. E. *Spectrochim. Acta. Part B* **1983**, *38*, 107.
7. Zhang, L.; Carnahan, J. W.; Winans, R. E.; Neil, P. H. *Anal. Chem.* **1991**, *63*, 212.
8. Michlewicz, K. G.; Carnahan, J. W. *Anal. Chem.* **1986**, *58*, 3122.
9. Ng, K. C.; Shen, W. *Anal. Chem.* **1986**, *58*, 2084.
10. Brown, P. G.; Haas, D. L.; Workman, J. M.; Caruso, J. A.; Fricke, F. L. *Anal. Chem.* **1987**, *59*, 1433.
11. Haas, D. L.; Caruso, J. A. *Anal. Chem.* **1984**, *56*, 2014.
12. Wilson, D. A.; Vickers, G. H.; Hieftje, G. M. *Anal. Chem.* **1987**, *59*, 1661.
13. Creed, J. T.; Davidson, T. M.; Shen, W.; Brown, P. G.; Caruso, J. A. *Spectrochim. Acta, Part B* **1989**, *44*, 909.
14. Park, C. J.; Pak, Y. N.; Lee, K. W. *Anal. Sci.* **1992**, *8*, 443.
15. Gustavsson, A. G. T. In *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*; Montaser, A.; Golightly, D. W., Ed.; VCH Publishers, New York, U. S. A. 1987; p 399.
16. Zander, A. T.; Hieftje, G. M. *Anal. Chem.* **1978**, *50*, 1257.
17. Pak, Y. N.; Koirtyohann, S. R. *Submitted to Spectrochim. Acta, Part B.*
18. Pak, Y. N.; Koirtyohann, S. R. *Submitted to J. Anal. At. Spectrom.*.
19. Haas, D. L.; Carnahan, J. W.; Caruso, J. A. *Appl. Spectrosc.* **1983**, *37*, 82.
20. Helmer, D.; Walters, J. P. *Appl. Spectrosc.* **1984**, *38*, 399.
21. Prell, L.; Koirtyohann, S. R. *Appl. Spectrosc.* **1988**, *42*, 1221.
22. Scheeline, A.; Norris, J. A.; Travis, J. C.; Devope, J. R.; Walters, J. P. *Spectrochim. Acta, Part B* **1981**, *36*, 373.
23. Ekimoff, D.; Walters, J. P. *Anal. Chem.* **1981**, *53*, 1644.

On the Stationary Probability Distributions for the Schlögl Model with the First Order Transition under the Influence of Singular Multiplicative Noise

Kyoung-Ran Kim, Dong J. Lee, Cheol-Ju Kim*, and Kook Joe Shin**

Department of Chemistry, National Fisheries University of Pusan, Pusan 608-737, Korea
**Department of Chemistry, Chonbuk National University, Chonbuk 560-742, Korea*
***Department of Chemistry, Seoul National University, Seoul 151-742, Korea*

Received March 21, 1994

For the Schlögl model with the first order transition under the influence of the multiplicative noise singular at the unstable steady state, the effects of the parameters on the stationary pobability distributions obtained by the Ito and Stratonovich methods are discussed and compared in detail.

Introduction

Recently, much attention has been paid to the stochastic processes with multiplicative random force in the fields of theoretical physics and chemistry.[1-5] Two of us[5] have discussed the stochastic phenomena for the Schlögl model with the first order transition driven by the multiplicative random force singular at the unstable steady state. The effects of the singularity on the stationary probability distribution based on the Stratonovich theory have been analyzed in detail. Then, the transition rate has been discussed from one stable steady state to the other stable steady state through the unstable steady state.

The Schlögl model exhibiting the first order transition in chemical reaction is given by[5-7]

$$A \xrightarrow{k_1} X,\ B+X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 3X+C,\ D+X \xrightarrow{k_3} E, \tag{1}$$

where k_i's are the rate constants, A, B and D are the concentrations of reactants and C and E denote those of products. The rate equation for X is given by the following equation while concentrations of other species being held constant

$$\frac{dX}{dt} = -Ck_{-2}\, X^3 + (k_2B - k_3D)X + k_1A \qquad (2)$$

Rewriting Eq. (2) in terms of the following scaled variables

$$\tau = Ck_{-2}t,\ \beta = (k_2B - k_3D)/Ck_{-2},\ \gamma = k_1A/Ck_{-2},$$

it reduces to

$$\frac{dX}{d\tau} = -X^3 + \beta X + \gamma \qquad (3)$$

For simplicity let $\gamma = 0$. When $\beta > 0$, there are three steady states, that is, $X_0 = \pm\beta^{1/2}$ and $X_0 = 0$ correspond to the stable and unstable states, respectively. In the case of $\beta < 0$, there exists only one stable steady state with $X_0 = 0$.

In order to discuss stochastic phenomena for the model let us write a Langevin equation with a multiplicative noise (random force)

$$\frac{dX}{d\tau} = -X^3 + \beta X + |X|^{\nu}\xi(\tau) \qquad (4)$$

with ν being an arbitrary number and the noise $\xi(\tau)$ being Gaussian and white

$$\langle\xi(\tau)\rangle = 0,\ \langle\xi(\tau)\xi(\tau')\rangle = 2D\ \delta(\tau - \tau'), \qquad (5)$$

where D is the diffusion coefficient and $\delta(\tau-\tau')$ is the Dirac delta function. The unstable steady state of the stochastic equation corresponds to that of the deterministic system. Eq. (4) can be rewritten in terms of $x = X - X_0 = X$, which is the deviation from the unstable steady state due to the multiplicative noise, as

$$\frac{dx}{d\tau} = -x^3 + \beta x + |X|^{\nu}\xi(\tau) \qquad (6)$$

It is well known that the Langevin equation in Eq. (6) is not completely defined since the noise is given by the delta function and we do not know which x value we have to take[8]. Ito and Stratonovich proposed further presriptions, respectively. In Ito's definition, the value of x before the jump should be taken for the probability distribution. On the other hand, the values of x before and after the jump are taken in average in Stratonovich's definition. Which definition we should take depends on the physical consideration. If we take both definitions, the Langevin equation may be transformed to the following Fokker-Planck equation(FPE)s, that is,

$$\frac{\partial}{\partial\tau}P(x,\tau) = -\frac{\partial}{\partial x}[(-x^3+\beta x)P(x,\tau)] + D\frac{\partial^2}{\partial x^2}[|x|^{2\nu}P(x,\tau)] \qquad (7a)$$

$$\frac{\partial}{\partial\tau}P(x,\tau) = -\frac{\partial}{\partial x}[(-x^3+\beta x)P(x,\tau)] + D\frac{\partial^2}{\partial x^2}\left\{|x|^{\nu}\frac{\partial}{\partial x}[|x|^{\nu}P(x,\tau)]\right\} \qquad (7b)$$

The equations of (7a) and (7b) correspond to the Ito and Stratonovich results, respectively.

The purpose of the present paper is to discuss the effects of the parameters on the stationary probabilities obtained by the Ito and Stratonovich methods and then compare the results.

In the next section the effects of the parameters on the stationary probability distribution are discussed in detail. Then the important results in the present papers are summerized.

The Stationary Probability Distribution

The stationary probability distributions of Eqs. (7) are given by the following expression:

$$P(x) = A\ \exp\{-V(x)/D\} \qquad (8)$$

where A is the normalization constant and $V(x)$ in the region of $x > 0$ are

$$V_I(x) = \begin{cases} \dfrac{1}{4-2\nu}x^{4-2\nu} - \dfrac{\beta}{2(1-\nu)}x^{2-2\nu} + 2\nu D\ \ln x & \text{for } \nu \neq 1 \text{ and } 2, \\ \dfrac{1}{2}x^2 + (2D-\beta)\ln x & \text{for } \nu = 1, \\ (1+4D)\ln x + \dfrac{\beta}{2x^2} & \text{for } \nu = 2. \end{cases} \qquad (9a)$$

$$V_S(x) = \begin{cases} \dfrac{1}{4-2\nu}x^{4-2\nu} - \dfrac{\beta}{2(1-\nu)}x^{2-2\nu} + \nu D\ \ln x & \text{for } \nu \neq 1 \text{ and } 2, \\ \dfrac{1}{2}x^2 + (D-\beta)\ln x & \text{for } \nu = 1, \\ (1+2D)\ln x + \dfrac{\beta}{2x^2} & \text{for } \nu = 2. \end{cases} \qquad (9b)$$

In Eqs. (9) the subscripts I and S in $V(x)$ denote that the probabilities are obtained from the Ito and Stratonovich methods, respectively. Comparing the above results, it can be easily seen that the Stratonovich result can be obtained from the Ito result by replacing $2\nu D$ in Eq. (9) by νD. Thus, from now on we shall only write the Ito results. The behavior of $V_I(x)$ in the region $x < 0$ can be easily obtained because of the symmetric property of the potential with respect to x. When $\nu = 1$, the probabilities by the Ito and Stratonovich methods in the case of $\beta > 2D(\beta < 2D)$ and $\beta > D(\beta < D)$ vanish (become infinite), respectively as $x \to 0$. The most serious difference between the probabilities occurs in the case of $D < \beta < 2D$. In this case the Ito probability diverges as $|x| \to 0$, while the Stratonovich probability becomes zero. The Ito result varies more sharply than the Stratonovich result and the maximal peak of the Ito probability approaches to the unstable steady state more closely. The comparison between the cases is shown in Figure 1.

If $\nu = 2$, the probability becomes zero, as $x \to 0$. The extrema of the probability in the cases of $\nu \neq 1$ and $\nu \neq 2$ may be obtained by solving the following algebraic equation

$$x^{4-2\nu} - \beta x^{2-2\nu} + 2\nu D = 0 \qquad (10)$$

Let us discuss two situations based on Eqs. (9) and (10).

(A) When $D \ll 1$ and $\nu < 0$, the maximal peak of $P_I(x)$ appears at

$$x_{I\max} \simeq \beta^{1/2}(1 - \nu D\beta^{\nu-2}). \qquad (11)$$

The multiplicative noise repels the probability from the unstable steady state. As ν approaches to 0, the probability near the unstable steady state varies sharply near $x = 0$ due

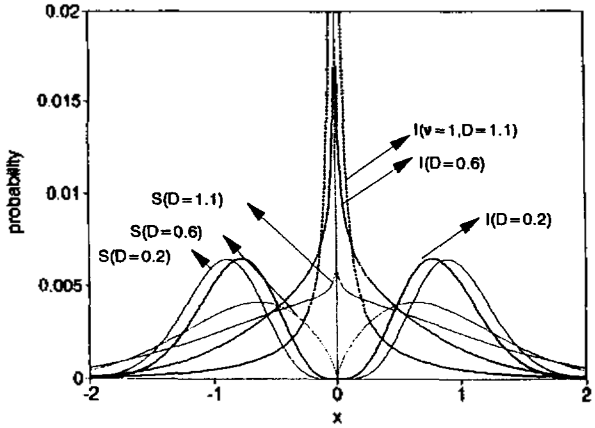

Figure 1. The comparison of probabilty distributions obtained by Ito and Stratonovich (denoted by I and S, respectively), when β and $\nu=1$.

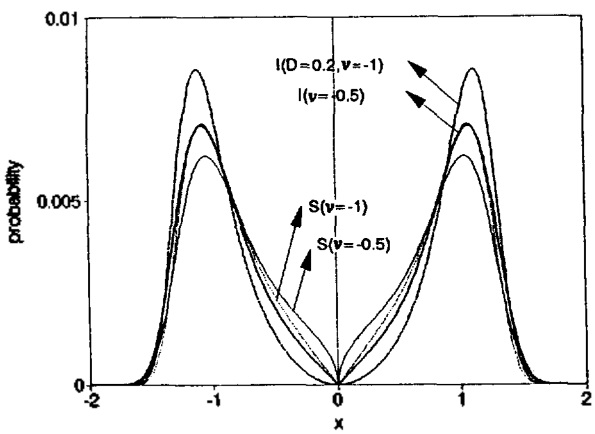

Figure 2. The Ito and Stratonovich probabilty distributions, when $\beta=1$, $D=0.2$ and $\nu<0$.

to the multiplicative noise. As ν becomes negatively larger, the probability becomes farther away from the unstable steady state. The multiplicative noise repels the Ito probability from the unstable steady state more strongly than the Stratonovich probability. Some examples are shown in Figure 2.

(B) If $D \ll 1$ and $0<\nu<1$. The maximal and minimal values of x are

$$x_{max} \simeq \beta^{1/2}(1-\nu D\beta^{\nu-2}),$$
$$x_{min} \simeq \left(\frac{2\nu D}{\beta}\right)^{1/(2-2\nu)}\left\{1-\frac{1}{(4-2\nu)-2\beta(1-\nu)\left(\frac{2\nu D}{\beta}\right)^{1/(\nu-1)}}\right\} \quad (12)$$

The multiplicative noise attracts the probability to the unstable steady state and a new minimal peak is produced due to the coupling between the noise and drift terms. As x approaches to 0, the Ito (Stratonovich) probabilities behave approximately as $1/x^{2\nu D}$ $(1/x^{\nu D})$ and become divergent at $x=0$ (See Figure 3). The divergence is caused by the multiplicative noise and is independent of the deterministic term.

The stochastic phenomena are completely different from the previous case, since the noise induces phase transitions.

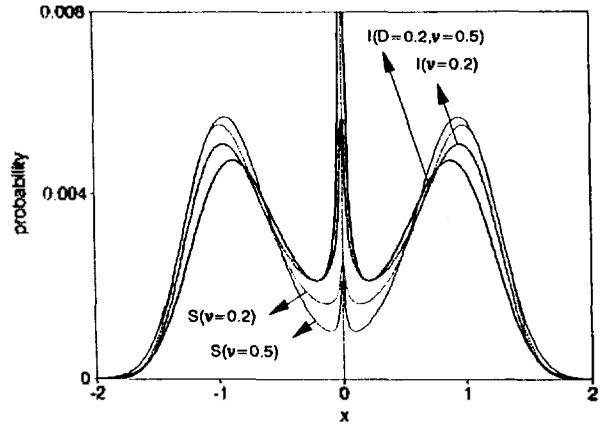

Figure 3. The Ito and Stratonovich probabilty distributions, when $\beta=1$, $D=0.2$ and $\nu>0$.

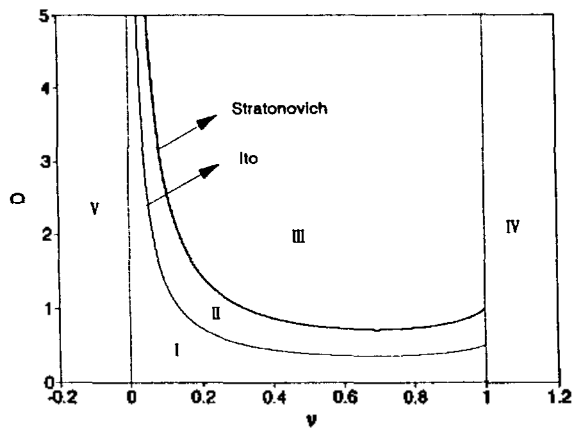

Figure 4. The Ito and Stratonovich phase diagrams, when $\beta=1$.

At the critical point the first and second derivatives of $V(x)$ with respect to x become zero. Thus, the critical values of x are

$$x_c=0, \ \left[\frac{2\beta(1-\nu_c)}{4-2\nu_c}\right]^{1/2} \quad (13)$$

The first case is trivial and let us neglect it. Then, the relation between the critical values of the diffusion coefficient and ν is

$$D_c=\frac{1}{2}\left(\frac{\beta}{2-\nu_c}\right)^{2-\nu_c}(1-\nu_c)^{1-\nu_c} \quad (14)$$

The bifurcation phase diagrams for the Ito and Stratonovich cases in the $\nu-D$ plane are shown in Figure 4. The straight lines $\nu=0$ and $\nu=1$ show the pitchfork bifurcation different from the saddle-node bifurcation obtained from Eq. (14).

Let us discuss the variation of the probability distributions when the system crosses the saddle-node bifurcation curve. At first, let us change the values of the diffusion coefficient by keeping $\nu=\nu_c=0.5$ (See Figure 5(a)). The critical values of D for the Ito and Stratonovich cases are 0.3849 and 0.7698, respectively. In the region I of Figure 4, the probability distributions satisfy the condition given in Eq. (12) and the multiplicative noise attracts the Ito distribution to the unsta-

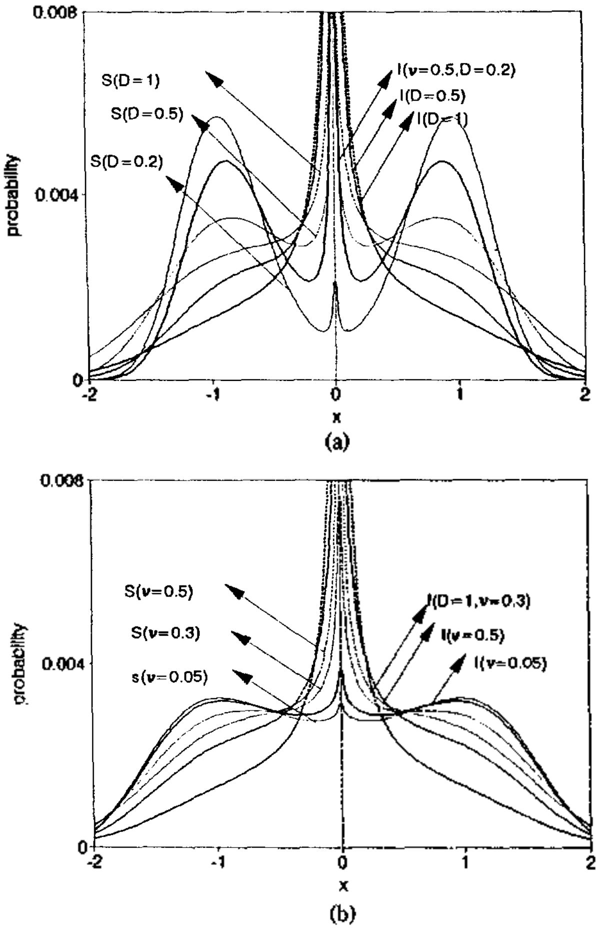

Figure 5. Dependence of the variation of the Ito and Stratonovich probabilty distributions on (a) D and (b) v, when the system crosses the saddle-point bifurcation curve.

ble state more strongly than the Stratonovich case. As $x \to 0$, the Ito probability distribution varies more sharply than the Stratonovich probability. When D is larger than the critical value of Stratonovich case, that is, the system is in the region III, the effect of the coupling can be neglected compared to the noise effect and thus, the Ito (Stratonovich) probability behaves approximatey as $1/x^{2vD}$ ($1/x^{vD}$). In the region II, the probabilities are quite different, since the main effect on the Ito probability is due to the multiplicative noise while the coupling between the noise and deterministic term plays the most important role for the Stratonovich probability. The probability distributions in the case of the constant D and varying v are just the same as those in the case of the constant v and changing D. An example is shown in Figure 5(b) by keeping $D_c=1$ and v=0.05, 0.3 and 0.5. As shown in the figures, the variation of the probability distributions crossing the saddle-node bifurcation curve is continuous.

The line v=0 is solely due to the multiplicative noise, while the v=1 line is due to the coupling between the noise and the linear part of the deterministic term. Let us consider the transition across the pitchfork bifurcation lines. The meeting points of the pitchfork bifurcation line v=1 and the Ito (Stratonovich) saddle-point bifurcation line is $D_c=0.5(1)$. In Figure 6(a) the phase transitions by crossing the pitchfork

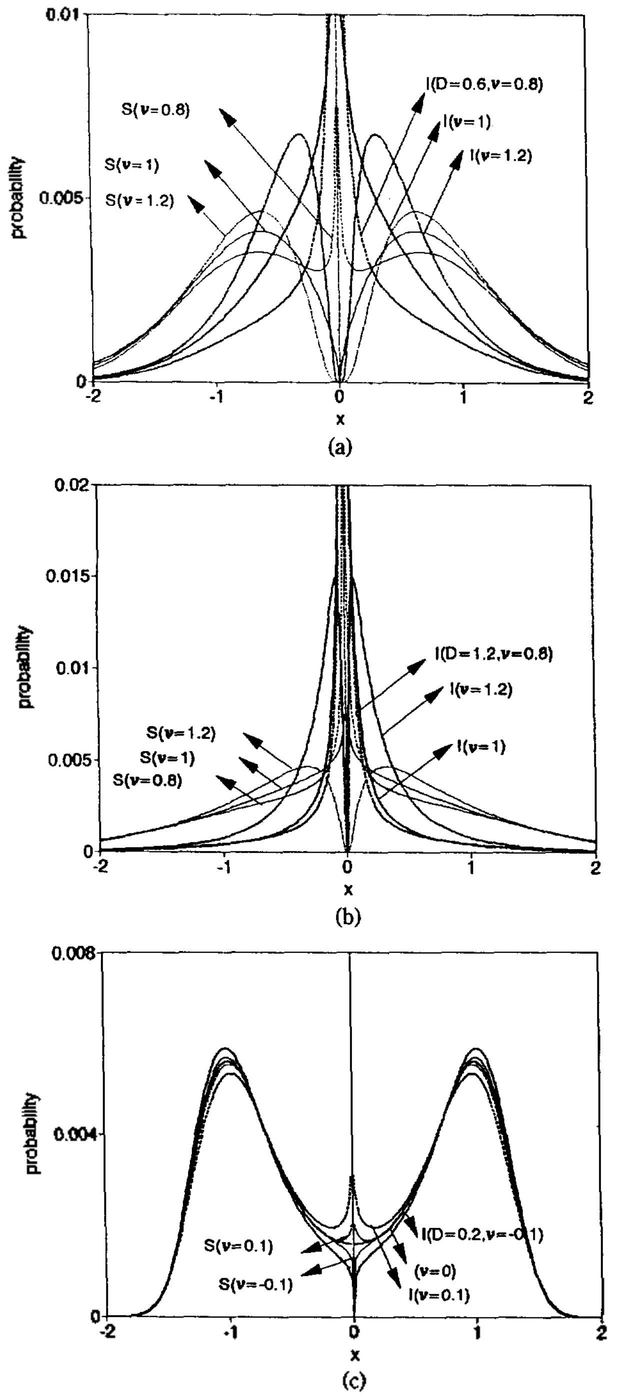

Figure 6. The variation of the Ito and Stratonovich probabilty distributions at D=(a) 0.6 and (b) 1.2, when the system crosses the pitchfork bifurcation line v=1 and (c) D=0.2, when the system crosses the pitchfork bifurcation line v=0.

bifurcation line are shown by letting $D=0.6$ and changing v=1.2, 1 and 0.8, respectively. In the region IV, the probability distributions have maximal peaks. However, the Ito case approaches to the unstable steady state more closely than the Stratonovich case. In the case of v=1 the comparison has been already discussed in the early part of this section. When v<1, the system is in the region II. Thus, the probability distributions are quite different, as already mentioned.

Some other examples are shown in Figures 6(b) and 6(c). As shown in the figures, the variation of the probability distributions by crossing the pitchfork bifurcation line is discontinuous.

Summary

We have compared the stationary probability distributions for the Schlögl model with the first order phase transition subjected to a multiplicative random force, which is singular at the deterministic unstable steady state by using the Ito and Statonovich methods for the stochastic process. Let us point out some important results.

(A) The multiplicative noise $|x|^{\nu}\,\xi(\tau)$ has an attracting (repelling) effect as $\nu>0$ ($\nu<0$), that is, it attracts (repels) the probability to (from) the unstable steady state. As $|\nu|$ increases, the attracting (repelling) force increases. The property competes with deterministic term in determining the stochastic properties of the system.

(B) When $\nu>0$, the stationary probability distribution becomes divergent at $x=0$. This result is clearly not realistic. Thus, a more realistic stochastic model should be proposed.

(C) The straight lines $\nu=0$ and $\nu=1$ give marginal situation, that is, the fluctuating intermediate undergoes the pitchfork bifurcation by crossing the lines and the variation of probability distributions becomes discontinuous, when the system undergoes the pitchfork phase transition.

(D) The diffusion coefficient with ν induces the saddle-node bifurcation in the case of $0<\nu<1$. Below the curve of the saddle-node bifurcation the coupling between the drift and noise terms plays the most important role. However, the multiplicative noise term becomes dominant above the curve. Thus, it is clear that the variation of probability distributions in the saddle-node transition is continuous.

(E) Even though the Ito and Stratonovich FPEs are based on the slight different definitions for the stochastic variable[8], some stochastic phenomena obtained from the equations are physically quite different, as shown in the previous section. Thus, it should be very careful to apply the Ito or Stratonovich FPE with multiplicative noise to an actual system.

In the following paper we shall discuss the stochastic phenomena for the Schlögl model with the second order transition subjected to the multiplicative noise singular at the unstable steady state.

Acknowledgments. This work was supported by a grant (No. BSRI-93-311) from the Basic Science Research Program, Ministry of Education of Korea, 1993.

References

1. Hu, G.; He, K. *Phys. Rev.* **1992**, *A45*, 5447.
2. Porra, J. M.; Masoliver, J.; Lindenberg, K. *Phys. Rev.* **1991**, *A44*, 4866.
3. Masoliver, J.; West, B.; Lindenberg, K. *Phys. Rev.* **1987**, *A35*, 3086.
4. Kus, K.; Wajnryb, E.; Wodkiewicz, K. *Phys. Rev.* **1991**, *A43*, 4167.
5. Kim, C. J.; Lee, D. J. *Bull. Korean Chem. Soc.* **1993**, *14*, 95.
6. Schlögl, F. *Z. Phys.* **1971**, *248*, 446; **1972**, *252*, 147.
7. Lee, D. J.; Ryu, M. H.; Lee, J. M. *Bull. Korean Chem. Soc.* **1985**, *6*, 91.
8. (a) Risken, H. *The Fokker-Planck Equations*; Springer-Verlag: New York, U. S. A., 1984; (b) Van Kampen, N. G. *Stochastic Processes in Physics and Chemistry*; North-Holland: Amsterdam, Netherland, 1981.

The Schlögl Model with the Second Order Transition Under the Influence of a Singular Multiplicative Random Force

Kyoung-Ran Kim, Dong J. Lee, Cheol-Ju Kim*, and Kook Joe Shin**

Department of Chemistry, National Fisheries University of Pusan 608-737, Korea
**Department of Chemistry, Chonbuk National University, Chonbuk 560-742, Korea*
***Department of Chemistry, Seoul National University, Seoul 151-742, Korea*
Received March 21, 1994

For the Schlögl model with the second order transition under the influence of the multiplicative noise singular at the unstable steady state, the detailed discussions are presented for various kinds of stochastic phenomena, such as the effects of parameters on stationary probability distribution, noise-induced phase transitions and escape rate.

Introduction

Recently, two of us[1] have discussed the stochastic phenomena for the Schlögl model with the first order transition driven by the multiplicative random force singular at the unstable steady state. The effects of the singularity on the stationary probability distribution have been analyzed in detail. Then, the transition rate has been discussed from one stable steady state to the other stable steady state through the unstable steady state. We[2] have also discussed and compared the effects of the parameters on the stationary probability distributions obtained by the Ito and Stratonovich