

- H. B. Kagan, *Tetrahedron Lett.*, **22**, 3959 (1981); (f) E. J. Corey and B. W. Erickson, *J. Org. Chem.*, **36**, 3553 (1971).
6. J. Verlhac, E. Chanson, B. Jousseume, and J. Quintard, *Tetrahedron Lett.*, **26**, 6075 (1985).
  7. (a) P. E. Fanta, *Chem. Rev.*, **64**, 613 (1964); (b) A. McKillop, L. F. Elsom, and E. C. Taylor, *J. Am. Chem. Soc.*, **90**, 2423 (1968).
  8. (a) M. Julia, M. Deuteil, C. Grard, and E. Kuutz, *Bull. Soc. Chim. France*, 2791 (1973); (b) F. R. Clark, R. O. Norman, and C. B. Thomas, *J. Chem. Soc. Perkin I*, 121 (1975).
  9. J. I. Kim and C. M. Ryu, *Bull. Korean Chem. Soc.*, **8**, 246 (1987).
  10. M. R. Kharrash, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).
  11. P. J. Harrington and L. S. Hegedus, *J. Org. Chem.*, **49**, 2657 (1984).
  12. D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972).
  13. B. Klein, *J. Am. Chem. Soc.*, **63**, 1474 (1941).
  14. H. Hatt, *J. Chem. Soc.*, 93 (1936).
  15. N. L. Bauld, *Tetrahedron Lett.*, 1841 (1963).
  16. F. D. Chattaway and E. A. Coulson, *J. Chem. Soc.*, 1361 (1928).
  17. H. Gilman and H. S. Broadbent, *J. Am. Chem. Soc.*, **63**, 1474 (1941).

## XPS Studies of Oxygen Adsorption on Polycrystalline Nickel surface (II)

Soon-Bo Lee, Jin-Hyo Boo, Kyoung-Hee Ham, and Woon-Sun Ahn\*

*Department of Chemistry, Sung Kyun Kwan University, Suwon 170*

Kwang-Soon Lee

*Department of Chemistry, Song Sim College For Women, Bucheon 150-71. Received October 19, 1987*

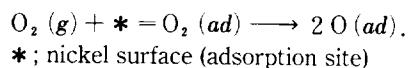
The isotherms of oxygen chemisorption on polycrystalline nickel surface are obtained at various temperatures between 298K and 523K from intensity measurement of O 1s xps peaks, and the activation energy of the chemisorption is estimated as a function of the coverage. The activation energy extrapolated to zero coverage is found to be -5.9kJ/mol. The negative activation energy can be taken as a strong implication of the propriety of a currently accepted chemisorption model, in which molecularly adsorbed precursor state is assumed to exist. The residence time of this precursor state is estimated by assuming a molecularly physisorbed state for the precursor state and assuming a pairwise interaction energy of Lennard-Jones 12-6 potential between an admolecule and each substrate nickel atom. The sticking coefficients are also calculated from the isotherms. The calculated results agree well with those obtained by others with different methods.

### Introduction

In our previous report of xps studies of oxygen adsorption on polycrystalline nickel surface<sup>1</sup>, it is reported that the O 1s xps peak at 530.2eV(binding energy) due to the dissociatively adsorbed oxygen atoms appears in the early stage of oxygen exposure at all the temperature range of experiment but the highest one at 523K. It is also reported that this dissociatively adsorbed oxygen species is responsible for the formation of p(2 × 2) and c(2 × 2) oxygen layer structures on Ni(100) surface. On further oxygen exposure, this species forms surface oxide layer, showing additional peaks at 531.3 eV and 529.7eV. The rate of this oxide layer formation decreases with increase in temperature. It is certain that an attempt to kinetic explanation for these observed results will augment the hitherto known knowledge of the oxygen chemisorption mechanism.

There have been a lot of studies on the mechanism of oxygen-nickel surface interaction systems, especially by means of AES and LEED<sup>2,3</sup> and photoelectron spectroscopy<sup>4,7</sup>. Most of the results are summarized in recent review articles<sup>8,9</sup>. For a reasonable explanation for these experimental

findings, it is generally assumed that oxygen is chemisorbed dissociatively through a molecularly adsorbed precursor state as following;



Brundle *et al*<sup>7</sup> observed that the sticking coefficient of oxygen molecule on the Ni(100) surface decreases linearly with the increasing oxygen coverage according to (1-4θ) at 300K, θ being the coverage. To explain the findings with the assumed model described above, they have further assumed that the molecularly adsorbed species has a so short residence time on the nickel surface that the rate of overall oxygen chemisorption is hardly influenced by temperature change at these elevated temperature range. On the other hand, they found a very high sticking coefficient at 77K, approaching almost unity up to higher coverage. They have assumed this temperature is low enough to hold the molecularly adsorbed species very long and thereby resulting in such a high sticking coefficient.

In spite of all these assumptions, no experimental evidence of the molecularly adsorbed species has been ever

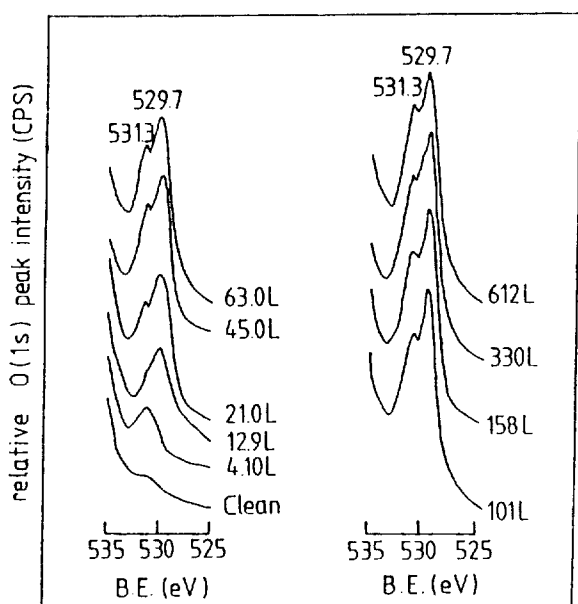


Figure 1. O(1s) photoelectron spectra with varying oxygen exposure at 298K.

reported. In this work, oxygen chemisorption isotherms are obtained from the xps spectra at various temperatures and activation energies for the chemisorption are calculated.

This work is to provide a more conclusive evidence for the currently accepted model of the oxygen-nickel interaction system.

## Results and Discussion

All the measurements are performed in a ultra high vacuum xps system (ESCA 750, Shimadzu Co., Japan) on which a quadrupole mass spectrometer (VG. Ltd., Masstorr FX, England) is attached. The pressure of the ESCA chamber is monitored with a BA ionization gauge. The details of the sample treatment and the calibration of binding energy spectra are described in the earlier papers<sup>1,10</sup>.

**(a) Activation Energy of the Initial Stage Adsorption.** X-ray photoelectron spectral peaks of O 1s resulting from the interaction of oxygen with polycrystalline nickel surface are measured at various temperatures, and one of the results at 298K are shown in Figure 1 as a function of oxygen exposure. The figure is quite similar to Figure 1 of the earlier report except there are more spectra at the intermediate exposures. The O 1s peak at 530.2eV is due to the dissociatively adsorbed oxygen as outlined in the introduction section, and the other two, at 531.3eV and 529.7eV, have been assigned to the non-stoichiometric NiO<sub>x</sub> and the surface NiO, respectively.<sup>1</sup>

The similar results are obtained at 373K and 423K. The result at 523K is however different a little in that the O 1s peak at 529.7eV only appears from the initial stage of the oxygen exposure, indicating the commencement of NiO layer formation from the early stage of adsorption. Assuming the area of each xps peak is proportional to the surface concentration of respective species, isotherms of the oxygen chemisorption can be obtained from the measured xps spectra. The resulting isotherms at 298K, 373K, 423K, and 523K are shown in Figure 2. All the isotherms in this figure show a knee bend near the peak area of ca 0.04, the scale being relative. From

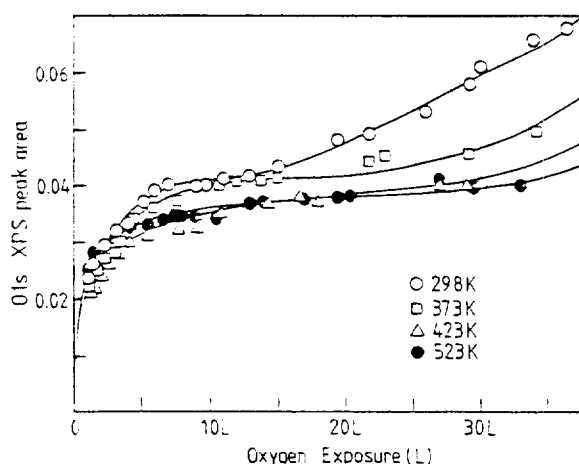


Figure 2. Isotherms of oxygen uptake at lower coverage on polycrystalline nickel surface at various temperatures.

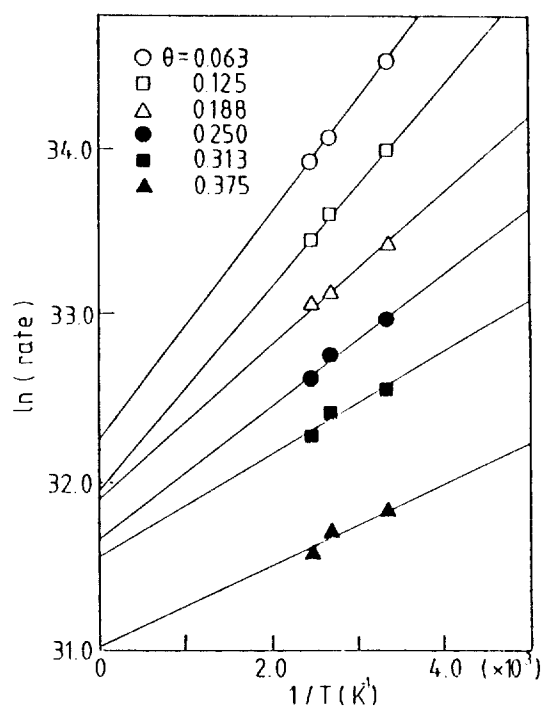


Figure 3. Arrhenius plots for the dissociative oxygen adsorption at various coverages.

the comparison of the isotherm at 298K obtained by this method with the one obtained from AES and LEED studies by Holloway *et al.*<sup>2,3</sup>, it is found that the peak area of 0.042 corresponds to the  $c(2 \times 2)$  LEED pattern. This peak area of 0.042, accordingly, is taken as the half monolayer coverage of oxygen atoms, that is  $8 \times 10^{14}$  atom/cm<sup>2</sup>. The isotherms of Figure 2 show that the oxygen exposure just needed to give this coverage increases with increasing temperature, being 12.9L at 298K, 23.0L at 373K, and 29.0L at 423K. This indicates that the rate of dissociative oxygen adsorption decreases with increasing temperature. This tendency can be attributed to the decrease in the residence time of the molecularly adsorbed species with increase in temperature.

Arrhenius plots at various oxygen coverages are made from the isotherms as shown in Figure 3. The activation energies for the chemisorption can be calculated from

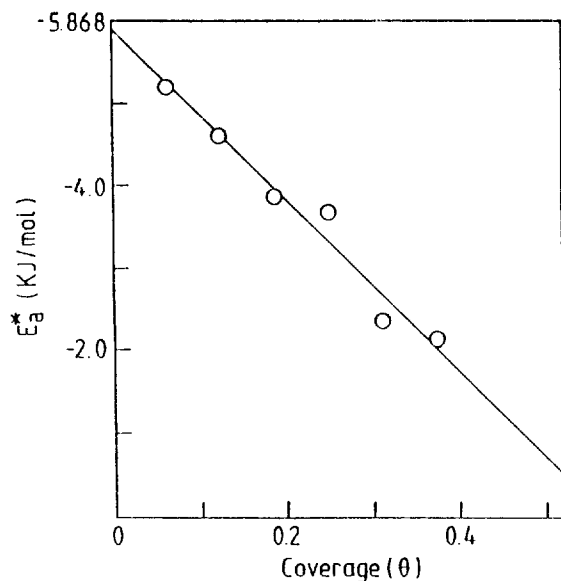


Figure 4. Activation energy of chemisorption as a function of oxygen coverage.

Table 1. Physisorption Energy of Oxygen Molecule on Nickel (111) Surface

16	17	16			
$\sigma_{gg}$	$\sigma_{ss}$	$\sigma_{gs}$	$\epsilon_{gs}(= \epsilon_{gg})$	$Z_{min}$	$U_{min}$
0.343	0.249	0.296	6.828	0.289	44.846

The unit of length is given in nm, and that of energy in kJ/mol.

slopes of the plots. The calculated activation energies plotted as a function of the oxygen coverage are shown in Figure 4. The activation energy extrapolated to zero coverage is -5.9 kJ/mol.

This activation energy is the one for the reaction,  $O_2(g) \rightarrow 2O(ad)$ , and the negative value should be taken as a strong implication of the propriety of a currently accepted model of molecularly adsorbed precursor state. Negative activation energies are observed in many gas-metal interaction systems, such as  $N_2$ -W(100),  $N_2$ -Fe(111), and  $O_2$ -Pt systems. All of these systems are known experimentally to make a dissociative adsorption through a molecularly adsorbed precursor state<sup>11-14</sup>.

**(b) Adsorption Energy of The Precursor State.** It is reasonable to assume the precursor state of molecularly adsorbed species as a physisorbed molecular species, and to estimate the adsorption energy of the precursor species by summing up pair-wise interaction energies between a physisorbed molecule and the nickel atoms. Using the Lennard-Jones 12-6 potential for the pair-wise interaction potential energy, the summation is carried out according to Steele's method<sup>15</sup>. Calculated results and parameters used therein are shown in Table 1. Nickel (111) plane is taken as the interaction surface, and a tertiary coordination position of the plane is taken as an adsorption site in this calculation. This plane is most densely packed, and thereby expected to give the largest interaction energy. Here,  $\sigma_{gs}$  is taken as an arithmetic mean of  $\sigma_{gg}$  and  $\sigma_{ss}$ , and  $\epsilon_{gs}$  is set equal to  $\epsilon_{gg}$  instead of taking a mean because  $\epsilon_{ss}$  is too high to give an absurdly high contribution to the mean value of  $\epsilon_{gs}$ . The  $Z_{min}$  is the calculated vertical height of the ad-molecule above the nickel

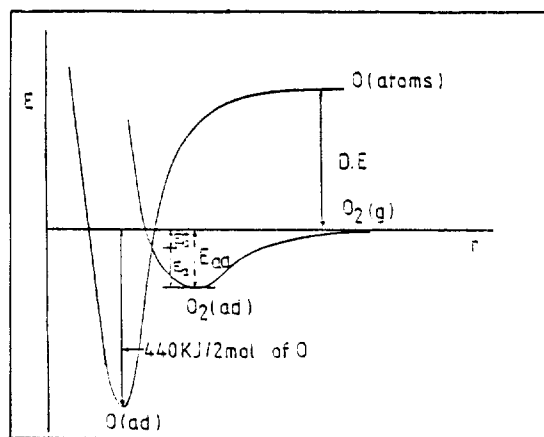


Figure 5. Potential energy diagram.

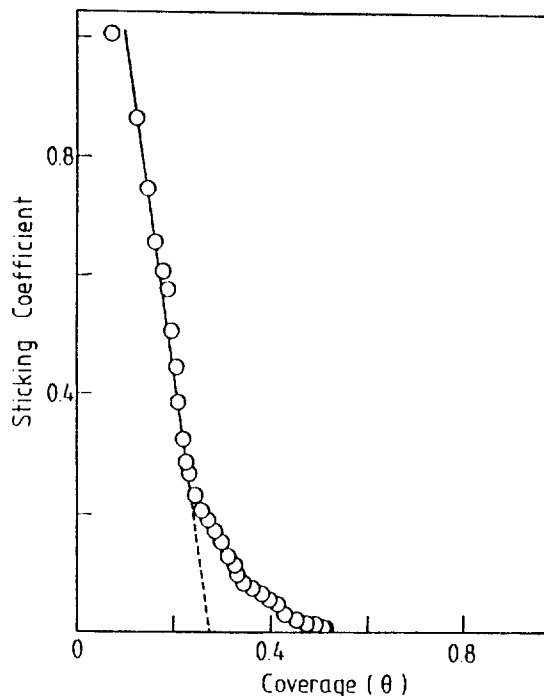


Figure 6. Sticking coefficient of oxygen chemisorption with varying coverages at 298K.

surface. The calculated energy minimum, which corresponds to the physisorption energy, is quite reasonable as a physisorption energy, and is much lower than the activation energy of the initial chemisorption.

**(c) Potential Energy Diagram.** The potential energy diagram based on the chemisorption model assumed currently is shown in Figure 5. The reaction coordinate is not to the scale, and the adsorption energy of  $O(ad)$  is taken from a literature value<sup>18</sup>. In compliance with this diagram, the precursor state species is assumed to pass into  $O(ad)$ , and the residence time of the species is calculated using the Frenkel equation,

$$\tau = \tau_o \exp(E_a/kT),$$

where,  $\tau_o$  is the time of oscillation of the molecules in the adsorbed state. Taking  $\tau_o = 10^{-3}$  sec, the value of  $\tau$  is calculated to be  $6.7 \times 10^{-7}$  sec at 298K,  $2.0 \times 10^{-7}$  sec at 323K, and  $6.5 \times 10^{-9}$  sec at 423K. The experimental failure in detecting the precursor state species can be attributed partly to this

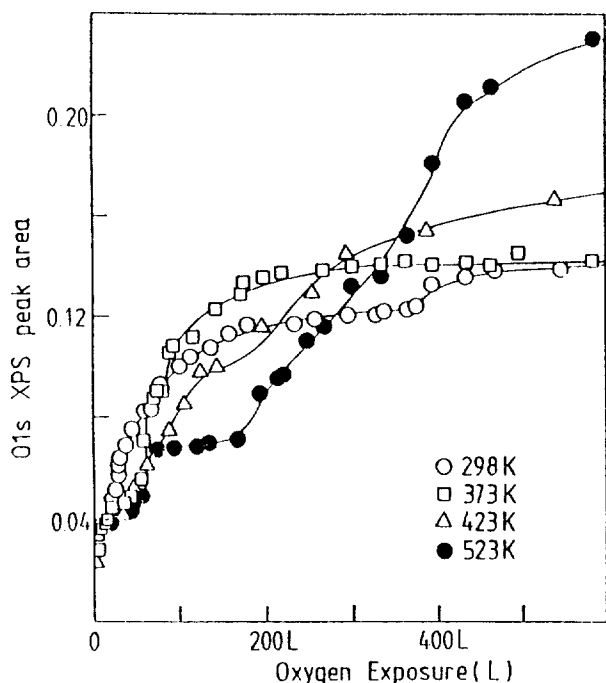


Figure 7. Full isotherms of oxygen uptake on polycrystalline nickel surface at various temperatures.

short residence time. The residence time increases, however, sharply with decreasing temperature. It would be  $2.6 \times 10^{13}$  sec at 77K, if the precursor state species underwent the same chemisorption path. Further work seems to be necessary to explain the experimental fact that nonmolecularly adsorbed species are detected yet in spite of such a long residence time.

**(d) Sticking Coefficient.** The number of chemisorbed oxygen atoms at any coverage can be calculated from the adsorption isotherms, as the 0.042 peak area of 298K isotherm in Figure 2 has been assumed previously to correspond to  $8 \times 10^{14}$  oxygen atom/cm<sup>2</sup>. Taking the residence time of the chemisorbed atoms infinite, the sticking coefficient of oxygen molecules can be calculated from the number of chemisorbed oxygen atoms. The results of calculation are shown in Figure 6. The value approaches unity at the initial stage, and decreases according to  $(1-4\theta)$  until the coverage reaches ca 0.2. This is a good agreement with the results of Brundle *et al.*<sup>7</sup> and Holloway *et al.*<sup>2</sup>. A long tailing beyond  $\theta = 0.2$  can be attributed to the effect of depleted adsorption sites.

**(e) Oxidation Process.** The full isotherms of oxygen uptake up to 600L exposure are obtained from the O 1s peak areas at the each experimental temperatures as shown in Figure 7. At the all temperatures other than 523K, only one O 1s peak appears at 530.2eV in the initial stage as shown in Figure 1, and this dissociative adsorption peak corresponds to the steep rising portion of the isotherms. Thus it is confident that the initial dissociative chemisorption takes place fairly rapidly. At 523K, however, O 1s peak appears at 529.7 eV at the initial stage instead of at 530.2eV. It is evident accordingly that the oxidation of the nickel surface commences directly with a moderate rate not through the dissociative adsorption.

Beyond the peak area of 0.042 through ca 0.085 (monolayer coverage region), O 1s peak appears at 529.7eV and 531.3eV. Whereas the former peak due to the surface NiO

increases rapidly in its intensity, the latter peak due to the non-stoichiometric NiO<sub>x</sub> remains almost constant irrespective of the increasing oxygen exposure. As assumed in our earlier paper, this non-stoichiometric NiO<sub>x</sub> is the resultant of oxygen atoms adsorbed on the surface NiO.

The oxygen exposures necessary to give a NiO monolayer in our work are 63L at 298K, 72L at 373K, 130L at 423K, and 150L at 523K. The results coincide with the findings of Holloway *et al.*<sup>2,3</sup> The isotherms of Figure 7 also show that the surface NiO layer continues to grow after the monolayer formation, reaching two layers at the all experimental temperature range, except at 523K at which three layers are reached. The rate of growth increases with increase in temperature. These results also agree with the findings of Holloway *et al.*<sup>2,3</sup> and Mitchell *et al.*<sup>5</sup>

## Conclusions

Though it is currently accepted that oxygen molecules chemisorb dissociatively on nickel surface through a molecularly adsorbed precursor state, no experimental evidence has been ever reported. The findings of the negative activation energy of oxygen chemisorption at the initial stage of adsorption of this work is believed to provide a firm evidence of this unidentified precursor state.

The adsorption energy of the precursor state molecular species is estimated from the calculated physisorption energy of oxygen molecules on Ni(111) surface. The obtained value of -44kJ/mol is quite reasonable, when compared to an experimental value of ca -40kJ/mol for O<sub>2</sub>-Pt system.<sup>11, 12</sup> The residence times of the precursor state species estimated in compliance with the above adsorption energy are temperature dependent. Brundle *et al.*<sup>7</sup> assumed a very short residence time qualitatively, and assumed further that the dissociative adsorption rate is hardly influenced by temperature change. They attributed the unsuccessful experimental detection of the precursor state species to this negligibly short residence time. The experiment of this work shows that the rate of the dissociative chemisorption decreases with increase in temperature, thereby resulting in a negative activation energy.

The chemisorption of oxygen proceeds relatively rapidly at the initial stage, where the dissociative chemisorption takes place, and then a moderately proceeding chemisorption follows to form an oxide monolayer. However at the highest temperature of this work, 523K, no dissociatively adsorbed oxygen species is found. The chemisorption takes place leading to the formation of the surface oxide layer from the initial stage, not passing through the dissociative adsorption. The formation of bulk nickel oxide seems to follow after two or three surface oxide layers are formed.

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## Reference

1. S. B. Lee, J. H. Boo and W. S. Ahn, *Bull. Korean Chem. Soc.*, to be published.
2. P. H. Holloway and J. B. Hudson, *Surf. Sci.*, **43**, 123 (1974).
3. P. H. Holloway and J. B. Hudson, *Surf. Sci.*, **43**, 141 (1974).

4. N. G. Krishnan, W. N. Delgass and W. D. Robertson, *Surf. Sci.*, **57**, 1 (1976).
5. D. F. Mitchell, P. B. Sewell and M. Cohen, *Surf. Sci.*, **61**, 355 (1976).
6. P. R. Notyon, T. L. Tapping and J. W. Goodale, *Surf. Sci.*, **65**, 13 (1977).
7. C. R. Brundle and H. Hopster, *J. Vac. Sci. Technol.*, **18(2)** 663 (1981).
8. P. H. Holloway, *J. Vac. Sci. Technol.*, **18(2)** 653 (1982).
9. C. R. Brundle, in "Aspects of the Kinetics and Dynamics of Surface Reactions", ed Uzi Landman. (American Institute of Physics, 1980) P. 57.
10. J. H. Boo, Thesis(M. S.) Sung Kyun Kwan Univ., 2 (1987).
11. S. K. Shi, J. M. White and R. L. Hance, *J. Phys. Chem.*, **84** 244 (1980).
12. J. L. Gland, *Surf. Sci.*, **93** 487 (1980).
13. D. A. King and M. G. Wells, *Proc. R. Soc. London, A* **339**, 245 (1974).
14. G. Ertl, S. B. Lee and M. Weiss, *Surf. Sci.*, **114**, 515 (1982).
15. W. A. Steel, Interaction of Gases with Solid Surfaces Chapt. 2, Pergamon, New York (1974).
16. J. O. Hirschfelder, C. E. Curtis, and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley & Sons, New York (1964).
17. A. B. Anderson, *J. Chem. Phys.*, **64**, 4046 (1976).
18. J. B. Benziger and E. Preston, *Surf. Sci.*, **141**, 567 (1984).

## The Time Correlation Functions of Concentration Fluctuations in the Lotka Model near the Oscillatory Marginal Steady State

Cheol-Ju Kim, Dong Jae Lee\*, Seuk Beum Ko† and Kook Joe Shin†

*Departments of Chemistry and †Chemical Education, Chonbuk National University, Chonbuk 520*

*\*Department of Applied Chemistry, National Fisheries University of Pusan, Pusan 608*

*†Department of Chemistry, Seoul National University, Seoul 151. Received October 20, 1987*

The time correlation functions of concentration fluctuations due to the random forces near the steady state are evaluated for a general two-component nonlinear chemical system by solving the corresponding two dimensional Fokker-Planck equation. The approximate method of solving the Fokker-Planck equation is based on the eigenfunction expansion and the corresponding eigenvalues for both the linear and nonlinear Fokker-Planck operators are obtained near the steady state. The general results are applied to the Lotka model near the oscillatory marginal steady state and the comparison is made between linear and nonlinear cases.

### Introduction

Various kinds of approximate methods<sup>1-7</sup>, such as size expansion<sup>1</sup>, time scaling<sup>2,3</sup>, mode-mode coupling<sup>4</sup>, dynamic renormalization<sup>5</sup> and etc.<sup>6,7</sup>, have been used to discuss the dynamic phenomena for a single component nonlinear chemical system, starting from a Langevin equation, Fokker-Planck equation or other equations. It is, however, much more complicated to obtain the dynamic properties for a multicomponent system than for a single component system.

The purpose of the present paper is to obtain the time correlation function of concentration fluctuations near a steady state for general two component nonlinear chemical system, assuming that chemical species obey a Langevin equation. The method to be used is the response theory<sup>7,9</sup>, which is one of the most effective methods. Then, applying the general results to a specific reaction model with instability, that is, the Lotka model<sup>10</sup>, we discuss the time correlation functions between the fluctuating parts of concentration near the oscillatory marginal stable steady state.

At first, we restrict ourselves to the linear Langevin equation. In order to discuss the time correlation function near a steady state(or equilibrium) we have to obtain the eigenvalue

and probability distribution of the linear Fokker-Planck equation. The easiest method in our opinion is the operator method as in quantum mechanics.<sup>7,8,11</sup> We diagonalize the linear Langevin equation with the aid of a suitable eigenvector<sup>3</sup> and obtain the corresponding linear Fokker-Planck equation. We introduce a function so that the Fokker-Planck equation is transformed into a time-dependent Schrödinger equation.<sup>7</sup> Using the creation and annihilation operators<sup>7,8,11</sup>, it can be shown that the probability distribution can be expressed in terms of the coupled Hermite polynomials. With the aid of the eigenfunction we may obtain the solvable recurrence formulae for the eigenvalues of the Fokker-Planck equation in any order of coupling. Then, we extend the linear theory to the nonlinear case to obtain the eigenvalue of the nonlinear Fokker-Planck equation. In the nonlinear case it is only possible to obtain the eigenvalue up to the first order of the coupling. Nevertheless, we may discuss the nonlinear effect on the time correlation functions near a steady state.

Finally, the general results for the correlation functions are applied to the Lotka model to obtain the correlation functions between the fluctuating parts due to the random forces at the oscillatory marginal steady state.