Statistical mechanics of polynuclear ring complexes with mixed-valence states by use of the Ising model

Koichi Aoki

Department of Applied Physics, Fukui University, 9-1, Bunkyo 3-chome, Fukui-shi, 910, Japan

Received 28 June 1994; in revised form 4 August 1994

Abstract

The correlated-walk theory is useful for estimating reversible current potential curves of a linear polynuclear complex with strongly electronic communication through a conjugated bridge. However, it falls short of a thermodynamic base because of the assumption of the local equilibrium at redox centers. In order to support the theory in the light of the statistical mechanics, the partition function of polynuclear ring complexes was derived by applying the eigenvalue technique of the Ising spin model. It contains the electrode potential, the number of redox centres and interaction energy of the nearest neighbor redox centres. The partition function is essentially equivalent to the generating function of the correlated-walk theory in so far as it is concerned with thermodynamic difference quantities such as the electrode potential and the configurational energy. Thus the microscopically local equilibrium on which the correlated-walk theory relays can reproduce the real equilibrium of the whole system. Expressions for the molar fraction of the oxidized centre, the internal energy and the entropy were obtained analytically as a function of the electrode potential and the nearest neighbour interaction. The internal energy varies with the electrode potential in the mixed-valence potential domain. The entropy is composed of the isomeric configurational contribution and the redox contribution due to different redox states.

Keywords: Statistical mechanics; Polynuclear ring complexes; Mixed-valence states; Ising model

1. Introduction

When a polynuclear complex has strongly electronic communication between redox centres through a conjugated bridge, it frequently takes a mixed-valence state at an intermediate redox level [1]. A well known example is a half integer of the valence number per molecule in the pyridine-bridged dinuclear ruthenium complex [2]. When a dinuclear complex has a well defined redox state, it shows two voltammetric waves [3–15]. A similar effect has been observed with conjugated dinitro compounds [13,14]. The difference in the peak potentials corresponds to the logarithm of the interaction energy [7–15], and has been reported as a comproportionation constant [3]. In contrast, a trinuclear complex can take 1/3 and 2/3 intermediate valence numbers per molecule, thus it exhibits three voltammetric waves [16,17]. A tetranuclear complex manifests four voltammetric waves [16] because of the possible states with every quarter valence number. Generally, an N-nuclear complex seems to take \( \frac{j}{N} \) redox states for \( 0 \leq j \leq N \), exhibiting \( N \) voltammetric waves unless there is any overlap of waves. In order to examine this prediction, the molar fraction of every species including isomers in the N-nuclear linear complex has been calculated as a function of the electrode potential by taking into account the closest neighbour interaction [18]. However, the prediction was negative: three and four waves were observed, respectively, for odd and even (\( N \geq 4 \)) values of \( N \); they coalesced into two waves for large values of \( N \). The reason why the \( N \) redox states degenerate is an interplay between the closest neighbour interaction and the generation of configurational isomers. Electrochemical data for a series of polynuclear ruthenium complexes with \( N \leq 6 \) [19] partly support the validity of the theory.

The calculation of the molar fraction was made by the application of the theory of the correlated walk [20]. When the oxidized (O) and the reduced (R) centres are located imaginarily on lattice sides parallel to the x-axis and the y-axis (see Fig. 1), respectively, a minimum distance track along lattice sides from the

0022-0728/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
SSDI 0022-0728(94)03690-X
Fig. 1. Coordinates of the correlated walk. Four lattice sites (●) denote an isomer of a trinuclear complex. The bold track is for R–O–O, which generates the ring by multiplying the probability by $q_1$.

origin up to a given lattice site can be regarded as an alignment of the redox centres [18]. A change in the stepping direction at a lattice site for a walker corresponds to a hetero-combination, whereas a straight step represents a homo-combination. Characteristics of the technique of the correlated walk are as follows:

(A) a minimum distance track on the lattice plane can stand uniquely for the arrangement of the redox centres;

(B) minimum distance tracks can cover all the possible configurational isomers, as exemplified by eight species for $N = 3$ in Fig. 1;

(C) each redox centre and each pair including the homo- and the hetero-combination are expressed by probabilities of taking their states as a function of the electrode potential and the interaction energies;

(D) the probability of forming an isomer is represented by a simple product of the probabilities of each redox centre and those of each pair in the isomer;

(E) the molar ratio of any isomer can readily be estimated from the probability as a function of the electrode potential;

The last feature may play a powerful role in analyzing current–potential curves.

The technique, however, includes an ambiguity in principle of statistical mechanics in that no partition function has been defined. More specifically, the correlated-walk theory assumes local equilibrium at each redox centre and each pair although the equilibrium should be established throughout whole the system by the intramolecular electron exchange and also the intermolecular exchange. Therefore, the state described by the correlated walk may deviate from the true equilibrium. In a previous paper [18], the validity was confirmed only for $N \leq 4$ by use of the conventional electrochemical equilibrium conditions.

The subject of the interacting redox reaction in the polynuclear complex is similar to the analysis of the one-dimensional Ising model [21] because the alignment of the two kinds of the redox centres resembles that of two spin vectors of the magnetism with the strong spin–spin interaction. However, correspondence is not straightforward, as can be seen in the following. The difference in the chemical status of the reduced and the oxidized centres gives rise to a difference between the R–R interaction energy and the O–O interaction energy [18]. In contrast, the direction of a spin vector is independent of chemical status and is rather operational. The electric field in the double layer is determined by the properties of supporting electrolytes rather than the complex, while magnetic spins experience a self-consistent magnetic field. The complex in solution is different in statistical ensembles from the magnetism because it is not only under the intramolecular equilibrium but also under the intermolecular equilibrium. In view of these differences, the analysis of the Ising model should be modified carefully into an electrochemical version. This paper describes a solution of the problem of the $N$-nuclear complex in order to establish the thermodynamic basis. From the comparison of the partition function of the Ising model with the generating function of the correlated walk, the limitation and validity of the correlated walk are discussed. Further, the dependence of the internal energy and the entropy on the electrode potential gives an electrochemical image of the configurational change.

2. Derivation

2.1. Electrochemical significance of partition function

The theory [18] of the correlated walk based on the local equilibrium at a redox centre is an approximation of the true electrochemical equilibrium, as described in Section 1. The degree of the approximation may be estimated by comparing the generating function of the correlated walk with the partition function of an ensemble of a number of complexes which give rise to the intermolecular charge transfer. However, the role in the partition function in the electrode reaction has not yet been elucidated, to the author's knowledge. In this Section, we consider the electrochemical significance of the partition function of polynuclear complexes.

We assume that the reversible one-electron transfer reaction $R \Rightarrow O + e^-$ occurs at each redox centre in the $N$-nuclear complex, independent of the interaction between redox centres. The O and the R centres experience the electric potential $\phi$, whereas the elec-
tron is subjected to the inner potential $\phi_M$ in the electrode phase. Let $\mu_R^0$ be the standard chemical potential of $R$, and $z_R$ be the charge number of $R$. Then the electrochemical potential of $R$ at unit activity is given by $\mu_{O,R} = \mu_R^0 + e z_R \phi$. The $O$ is always associated with the electron. Letting $\mu_{O,e}$ be the sum of the electrochemical potentials of the $O$ and the electron, we have $\mu_{O,e} = \mu_O^0 + \mu_e^0 + e z_e (\phi - \phi_M)$. Obviously, it follows that $z_O = z_R = 1$. It is assumed that the interaction energy of two neighbouring oxidized centres is equal to that of two neighbouring reduced centres, i.e., $U_{OO} = U_{RR}$. Let $u_{RO}$ be the interaction energy between $O$ and $R$. Then, a redox state of the complex depends not only on the numbers of $O$ and $R$ but also on the configurational arrangement of the redox centres. The Hamiltonian for a given state is represented by a combination of $\mu_{O,e}, \mu_R, u_{OO}$ and $u_{RO}$. For example, the complex $O$–$O$–$R$–$O$–$R$–$R$–$O$ has the state of $H = 3\mu_R + 4\mu_{O,e} + 2u_{OO} + 4u_{RO}$.

The ensemble of $N$-nuclear molecules treated here is composed of $n_j$ molecules of the $j$th species having Hamiltonian $H_j$, where $1 \leq j \leq J$ ($J$ is the maximum number of the available states). The probability of the event of taking the value $H_j$ is $\exp(-H_j/kT)$, where $k$ is Boltzmann’s constant and $T$ is the absolute temperature. Since $n_j$ molecules are indistinguishable, the partition function of the ensemble is given by

$$Z_N = \frac{n!}{n_1!n_2!\cdots n_J!} \exp(-n_1\beta H_1) \cdots \exp(-n_J\beta H_J)$$

(1)

where $n = \sum n_j$ and $\beta = 1/kT$. According to the conventional definition of the chemical potential $(-kT \ln Z_N/n)$, the differentiation of Eq. (1) yields

$$\overline{\mu}_j = -kT \frac{\partial \ln Z_j}{\partial n_j} = H_j + kT \ln(n_j/n)$$

(2)

Applying the equilibrium conditions, $\overline{\mu}_1 = \overline{\mu}_2 = \cdots = \overline{\mu}_j$ to Eq. (2), we obtain

$$n_j/n = \exp[\beta(\overline{\mu}_j - H_j)]$$

(3)

We assign all the reduced centres to the $J$th species, i.e.,

$$H_J = N\mu_R^0 + (N-1)u_{RO} + Nez_R \phi$$

(4)

Inserting Eq. (3) into $\sum n_j/n = 1$ and multiplying it by $\exp(-\beta \overline{\mu}_j)$, we have

$$Z_N = \sum_{j=1}^J \exp(-\beta H_j) = \exp(-\beta \overline{\mu}_J)$$

(5)

This is the partition function per $N$-nuclear complex. For small values of $N$ or $J$, the one-molecular partition function seems to exhibit a discrete variation of thermodynamic variables when the charge or the configuration alters stepwise. It will be shown, however, in Section 3 that the discreteness is smoothed by the electrode potential.

In general, the equilibrium potential corresponds to a difference in the Gibbs energy relative to a given species. If the $J$th species is regarded as the reference, Eq. (5) is rewritten as

$$Z_N \exp(\beta H_J) = \sum_{j=1}^J \exp[-\beta(H_j - H_J)]$$

(6)

A general term of $H_j$ can be expressed by

$$H_j = m_1(\mu_O^0 + \mu_e^0) + m_2 \mu_R + m_3 u_{RO} + m_4 u_{OO} + e \phi(m_1 z_O + m_2 z_R) - m_1 \phi_M$$

(7)

Here $m_1, m_2, m_3$ and $m_4$ are non-negative integers such that $m_1 + m_2 = N$ and $m_3 + m_4 = N - 1$, depending not only on the degree of the oxidation but also on the aligned configuration of the redox centres. Inserting Eq. (7) into Eq. (6) and defining the difference of the interaction energy as

$$b = \mu_{RR} - \mu_{RO} = U_{RR} - U_{RO}$$

(8)

and the dimensionless potential as

$$\xi = \left[ e(\phi_M - \phi) - (\mu_O^0 + \mu_e^0 - \mu_R^0) \right] / kT$$

(9)

we can reduce $\beta(H_j - H_J)$ to $-m_1 \xi - m_3 \beta u_1$. Denoting a set of all the possible combinations of $m_1$ and $m_3$ as $\{m_1, m_3\}$, we rewrite Eq. (6) as

$$Z_N \exp(\beta H_J) = \sum_{\{m_1, m_3\}} \exp(m_1 \xi + m_3 \beta u_1)$$

(10)

Since Eq. (10) is expressed in terms of $\xi$, we can refer it as an electrochemical partition function. If the exhaustively oxidized complex is assigned to the $J$th species instead of Eq. (4), Eq. (6) is reduced to the summation of $\exp(-m_2 \xi + m_3 \beta u_1)$ with respect to all the combinations $\{m_2, m_3\}$. Whatever substance may be assigned to the $J$th species, the functional form of Eq. (10) is retained with respect to $\xi$ and $u_1$. Therefore, the electrochemically significant partition function is a product of the canonical partition function by the Boltzmann factor for an arbitrary reference species.

2.2. Electrochemical interpretation of Ising model

In this section, a redox state of a polynuclear ring complex is analysed by means of the eigenvalue method [22], which was developed for the problem of the one-dimensional Ising spins located in an external magnetic field. The reason for treating the ring complex (1 and 2 in Fig. 1) instead of a linear complex is to prevent the asymmetric mathematical complication of the partition function owing to the terminal effect of the linear complex. The contribution of the terminal...
effect may be about $2/N$ of a thermodynamic property, and hence the ring complex can be regarded as a model of the linear complex for large values of $N$.

We introduce an indicator variable $s_i$ ($1 \leq i \leq N$) at the $i$th redox center on the ring. The variable can take values of either 1 or -1, representing the reduced or the oxidized state. We rewrite the Hamiltonian per molecule as

$$H = (\bar{\mu}_{\text{Oe}} + \bar{\mu}_{R} + u_{OO} + u_{RO}) N/2 + \left[ (\bar{\mu}_{\text{Oe}} - \bar{\mu}_{R}) / 2 \right] \times \sum_{i=1}^{N} s_i + \left( u_{1/2} / 2 \right) \sum_{i=1}^{N} s_is_{i+1}$$

(11)

where $s_{N+1} = s_1$. This is essentially the same as the $H_j$ defined in Section 2.1. The canonical partition function of Eq. (5) is expressed by summation of $e^{-\beta H}$ for all permissible values of $s_i$ (-1 or 1):

$$Z_N = \sum_{s_1=-1}^{1} \sum_{s_2=-1}^{1} \cdots \sum_{s_N=-1}^{1} e^{-\beta H}$$

(12)

By the use of the new function

$$g(s_i, s_{i+1}) = \exp \left[ -\frac{\beta}{4} (\bar{\mu}_{\text{Oe}} - \bar{\mu}_{R}) (s_i + s_{i+1}) - \frac{\beta}{2} u_1 s_i s_{i+1} \right]$$

$$= \exp \left[ \frac{\xi}{4} (s_i + s_{i+1}) - \frac{\beta}{2} u_1 s_i s_{i+1} \right]$$

(13)

Eq. (12) can be rewritten as

$$Z_N = \exp \left[ -\frac{N}{2} \beta (\bar{\mu}_{\text{Oe}} + \bar{\mu}_{R} + u_{OO} + u_{RO}) \right]$$

$$\times \sum_{s_1=-1}^{1} \sum_{s_2=-1}^{1} \cdots \sum_{s_N=-1}^{1} g(s_1, s_2) g(s_2, s_3) \cdots$$

$$\times g(s_{N-1}, s_N) g(s_N, s_1)$$

(14)

The simplest example of $Z_N$ is for $N = 2$:

$$Z_{N=2} = \exp \left[ -\beta (\bar{\mu}_{\text{Oe}} + \bar{\mu}_{R} + u_{OO} + u_{RO}) \right]$$

$$\times \sum_{s_1=-1}^{1} \sum_{s_2=-1}^{1} g(s_1, s_2) g(s_2, s_1)$$

$$= \exp \left[ -\beta (\bar{\mu}_{\text{Oe}} + \bar{\mu}_{R} + u_{OO} + u_{RO}) \right]$$

$$\times \left[ g(1, 1)^2 + 2g(1, -1)g(-1, 1) + g(-1, -1)^2 \right]$$

$$= \exp \left[ -2\beta (\bar{\mu}_{\text{Oe}} + u_{OO}) \right]$$

$$+ 2 \exp \left[ -\beta (\bar{\mu}_{\text{Oe}} + \bar{\mu}_{R} + 2u_{RO}) \right]$$

$$+ \exp \left[ -2\beta (\bar{\mu}_{R} + u_{RO}) \right]$$

(15)

This agrees with the form obtained from Eqs. (5) and (7).

We introduce the matrix

$$T = \begin{pmatrix} g(1, 1) & g(1, -1) \\ g(-1, 1) & g(-1, -1) \end{pmatrix}$$

$$= \begin{pmatrix} \exp(\xi/2 - \beta u_{1/2}) & \exp(\beta u_{1/2}) \\ \exp(\beta u_{1/2}) & \exp(-\xi/2 - \beta u_{1/2}) \end{pmatrix}$$

(16)

Since the diagonal elements of $T^2$ are $g(1, 1)^2 + g(1, -1)g(-1, 1)$ and $g(-1, 1)g(1, -1) + g(-1, -1)^2$, their sum is identical with the three terms in the braces, is Eq. (15). By mathematical induction, the sum of the diagonal elements of $T^N$, denoted by trace $(T^N)$, is equivalent to the summation of Eq. (14). Diagonal terms can be evaluated as eigenvalues by means of the Unitary transformation [23] of $T^N$. Let $\lambda$ be the eigenvalue of $T$. Then,

$$Z_N = \exp \left[ -\frac{N}{2} \beta (\bar{\mu}_{\text{Oe}} + \bar{\mu}_{R} + u_{OO} + u_{RO}) \right] (\lambda_+^N + \lambda_-^N)$$

(19)

Extracting the term $\exp(-\beta H_j) = \exp[-N\beta(\bar{\mu}_{R} + u_{RO})]$ from Eq. (19), we can rewrite Eq. (19) as

$$Z_N = \exp(-\beta H_j) \left( \frac{1 + \exp(\xi)}{2} \right)^N \left( (1 + \chi)^N + (1 - \chi)^N \right)$$

(20)

where

$$\chi = \sqrt{1 - \exp(2\beta u_1)} \tanh^2(\xi/2) + \exp(2\beta u_1)$$

(21)

This is an electrochemical partition function of the polynuclear ring complex, varying with $\xi$, $\beta u_1$ and $N$. It allows us to evaluate all the thermodynamic properties, as will be shown in Section 3.

2.3. Correspondence between the Ising analysis and the correlated-walk theory

The generating function of the correlated-walk theory is composed of summation of the products of the probabilities of all the configurations of the redox centres under the local equilibrium. Since a redox
centre can take the alternative of the O or the R state depending on whether it is lower or higher than the Fermi level ($\mu_e^O + \mu_e^R - \mu_o^R$), the probability of taking the O state obeys the Fermi distribution [24]:

$$P_1 = \frac{1}{1 + e^{-\beta u_1}}$$  \hspace{1cm} (22)

The reduced state corresponds to the complement $q = 1/(1 + e^{\beta u_1})$. Let $p_1$ and $q_1$ be, respectively, the probability of taking the O-O and the O-R (see Fig. 1). In a thermal bath, $p_1$ and $q_1$ have the Boltzmann factor: $p_1 = k_1 \exp(-\beta u_{oo})$ and $q_1 = k_1 \exp(-\beta u_{ro})$ with a constant $k_1$. Since $p_1 + q_1 = 1$, $p_1$ and $q_1$ are given by

$$p_1 = \frac{1}{1 + \exp(\beta u_1)} \quad q_1 = \frac{1}{1 + \exp(-\beta u_1)}$$  \hspace{1cm} (23)

We also define $p_2$ or $q_2$ as the probability of taking, respectively, the R-O and the R-R. Obviously we have $p_2 = q_1$. Since $u_{oo} = u_{rr}$, it follows that $p_1 = q_2$. Taking into account that the linear complex with the terminal condition $s_I = s_{N+1}$ becomes a ring, we can substitute the ring for the linear complex by adding an inter-terminal connecting term $p_1$, $q_1$, $p_2$ or $q_2$ to the series of a product of probabilities. For example, probability $q_2p_2p_1q_1$ representing the R-O-O is modified by the $q_1q_2p_2p_1$ for ring polymer 2 in Fig. 1, where $q_1$ plays a role in connecting the right and the left ends of the linear polymer. Testing the components of the probabilities of various ring polymers, we found that the probability always consisted of a combination of $p_1p_2$, $p_2p_1$, $q_1q_2$, and $q_2q_1$.

The summation of all the permissible probabilities in a dinuclear complex is given by

$$\Phi(2) = p^2p_1^2 + 2p_2p_1q_1 + q^2q_2^2$$  \hspace{1cm} (24)

Applying the concept of the eigenvalue method to Eq. (24), we find that $\Phi(2)$ is equal to the trace of the square of the $2 \times 2$ matrix whose elements are $p_1$, $q_1$, $p_2$, and $q_2$. According to the mathematical induction, $\Phi(N)$ can be expressed by

$$\Phi(N) = \text{trace} \left( \begin{array}{cc} p_1 & q_1 \\ p_2 & q_2 \end{array} \right)^N$$  \hspace{1cm} (25)

Eigenvalues $\alpha$ for $\Phi(1)$ are given by the solution of

$$(p_1 - \alpha)(q_2 - \alpha) - p_2q_1 = 0$$

$$\alpha_{\pm} = \frac{1}{2} \left[ p_1 + q_2 \pm \sqrt{(p_1 - q_2)^2 + 4p_2q_1} \right]$$  \hspace{1cm} (26)

Extracting $\sqrt{p_2q_1}$ deliberately from $\alpha_{\pm}$ and using relations $p/q = e^{\xi}$ and $p_1/q_1 = q_2/p_2 = \exp(-\beta u_1)$, we have

$$\alpha_{\pm} = \sqrt{p_2q_1} \left[ \exp(-\beta u_1/2) \cosh(\xi/2) \pm \sqrt{\exp(-\beta u_1) \sinh^2(\xi/2) + \exp(\beta u_1)} \right]$$  \hspace{1cm} (27)

Then $\Phi(N)$ is given by

$$\Phi(N) = \alpha^N_{\pm} + \alpha^{-N}_{\pm} = (p_2q_1)^{N/2}(\lambda^N_{\pm} + \lambda^{-N}_{\pm})$$  \hspace{1cm} (28)

Eliminating $\lambda_{\pm}$ from Eqs. (19) and (28), we obtain the relation between $Z_N$ and $\Phi(N)$:

$$Z_N = \frac{\left[ 4 \cosh \frac{\zeta}{2} \cosh \frac{\beta u_1}{2} \times \exp \left[ -\frac{\beta}{2} (\mu_e^o + \mu_e^r + u_{oo} + u_{ro}) \right] \right]^N}{\Phi(N)}$$

$$\Phi(N) = \exp(-\beta H_J)(1 + e^{\xi})^N \{1 + \exp(\beta u_1)\}^N \Phi(N)$$  \hspace{1cm} (29)

This is the correspondence between the Ising analysis and the correlated-walk theory.

Since the term $\exp(-\beta H_J)(1 + e^{\xi})^N\{1 + \exp(-\beta u_1)\}^N$ contains no factor of distinguishing isomers, all the configurational information is concentrated in $\Phi(N)$. In other words, $\Phi(N)$ can be regarded as one of the partition functions that characterize the configurational or isomeric interaction. We can propose another feature of the correlated-walk theory that should be added to (A)-(E) in Section 1:

(F) $\Phi(N)$ is equivalent to the partition function so far as it is concerned with isomeric configuration.

This is a main target of this report. Another feature is

(G) the microscopically local equilibrium condition expressed by the Fermi probability is equivalent to the macroscopically real equilibrium for the isomeric configuration.

The equivalence confirms that the product of local probabilities allows us to evaluate all the thermodynamic quantities.

3. Thermodynamic properties

3.1 Molar fraction of oxidized centres

The electrochemically interesting quantity is the sum of the molar fraction $x_O$ of the oxidized centres, which is responsible for the shape of current–potential curves. In a previous paper [18], $x_O$ was derived from the particular feature of the generating function $\Psi$ (not from $\Phi(N)$). Since the derivation was inherent in the functional form of $\Psi$, it cannot be applied to the partition function. We now obtain the expression for $x_O$ from the partition function by another method and discuss variations of $x_O$ with $\xi$.

Let $m(j)$ be the number of the oxidized centres in
the jth molecule. Then the sum of the molar fraction is expressed by

\[ x_0 = \sum_{j=1}^{J} m(j) \exp(-\beta H_j)/(NZ_N) \]

\[ = \frac{\sum_{j=1}^{J} m(j) \exp(-\beta(H_j - H_j))}{N\left[(1 + \exp(\xi))/2\right]^N[(1 + \chi)^N + (1 - \chi)^N]} \tag{30} \]

where Eq. (20) has been employed. Since \( \exp(-\beta(H_j - H_j)) \) includes \( \exp(e^\zeta) \), its differentiation with respect to \( \zeta \) can induce \( m \) as a pre-exponential term. Thus Eq. (30) is rewritten as

\[ x_0 = \sum_{j=1}^{J} \left( \frac{\delta \exp(-\beta(H_j - H_j))}{\delta \zeta} \right) \]

\[ = \frac{1}{N(1 + \exp(\xi)/2)^N[(1 + \chi)^N + (1 - \chi)^N]} \tag{31} \]

Exchanging the order of the differentiation and the summation gives the equation for the molar fraction due to the partition function:

\[ x_0 = \frac{\partial \ln Z_N}{N\partial \zeta} \tag{32} \]

Substituting \( \Phi(N) \) in Eq. (29) for \( Z_N \) results in an equation in terms of the generating function:

\[ x_0 = \frac{1}{1 + \exp(\xi)} + \frac{\partial \ln \Phi(N)}{N\partial \zeta} \tag{33} \]

Since the derivation contains no operation with respect to the configuration, Eqs. (31) and (32) hold for any functional form of \( Z_N \) or \( \Phi(N) \). Carrying out the differentiation of \( \ln Z_N \) or \( \ln \Phi(N) \), we have

\[ x_0 = \frac{1}{1 + \exp(\xi)} \]

\[ + \frac{(1 + \chi)^{N-1} - (1 - \chi)^{N-1}}{(1 + \chi)^N + (1 - \chi)^N} \frac{1 - \chi^2}{2\chi} \tanh(\xi/2) \tag{34} \]

Limiting behaviour is discussed here. As \( \xi \to \pm \infty \), the Taylor expansion of Eq. (21) gives \( \chi^2 = 1 + 4\exp(2\beta u_1) - 1 \). Then \( 1 + \chi \) and \( 1 - \chi \) tend, respectively, to 2 and 0. Since \( \tanh(\xi/2) \) approaches \( \pm 1 \) as for \( \xi \to \pm \infty \), we have

\[ x_0 \approx \frac{1}{1 + \exp(\xi)} \times \left[ \exp(2\beta u_1) - 1 \right] \exp(\xi) \tag{35} \]

When \( \beta u_1 \) is large, it follows that \( x_0 \approx 1 - \exp(2\beta u_1 - \xi) \) for \( \xi \to \infty \) and that \( x_0 \approx \exp(2\beta u_1 + \xi) \) for \( \xi \to -\infty \). Therefore, it is in the domain \( \Delta \xi = 4\beta u_1 \) that the molar fraction varies largely from 0 to 1. Since \( \tanh(0) = 0 \), we have obviously \( x_0 = 1/2 \) at \( \zeta = 0 \).

It is interesting to estimate \( \partial x_0/\partial \zeta \) at \( \zeta = 0 \). Carrying out the differentiation, we obtain

\[ \left( \frac{\partial x_0}{\partial \zeta} \right)_{\zeta=0} = \frac{1}{4} \left( \frac{(1 + x_0)^N - (1 - x_0)^N}{(1 + x_0)^N + (1 - x_0)^N} \right) \sinh(\beta u_1) \tag{36} \]

where \( x_0 = (\chi x_0 - \exp(\beta u_1)) \). For large values of \( \beta u_1 \), the sign of \( (1 - x_0)^N \) depends on whether \( N \) is even or odd. By use of the Taylor expansion of \( (1 \pm x_0)^N \), we have

\[ \left( \frac{\partial x_0}{\partial \zeta} \right)_{\zeta=0} \approx \frac{\exp(-2\beta u_1)}{4N} \to 0 \text{ for even } N \tag{37} \]

\[ \left( \frac{\partial x_0}{\partial \zeta} \right)_{\zeta=0} \approx \frac{1 - \exp(-2\beta u_1)}{4N} \to 1 \text{ for odd } N \tag{38} \]

Therefore the shape of the \( x_0 \) vs. potential curves for even \( N \) is different from that for odd \( N \), as in the linear polymers [18].

Variations of \( x_0 \) with the potential were computed for various values of \( N \) and \( \beta u_1 \) from Eq. (34), and were plotted in Fig. 2 (solid lines) together with those of the corresponding linear complexes (dashed lines) [18]. When \( \beta u_1 > 2 \), two sigmoids were obtained for even \( N \) whereas there were three sigmoids for odd \( N \). When \( N = 2 \), the interaction energy has been counted twice, as seen from Eq. (15). Therefore, the curve at \( N = 2 \) is for \( 2\beta u_1 \). The curve for \( N = 3 \) shows the potential difference from the curve of the linear complex in \( x_0 < 1/3 \) and \( x_0 > 2/3 \). Since the difference 1.10 is close to \( \ln 3 \), it may be an entropic effect for the rotational symmetry. The entropic effect due to the redox symmetry has been discussed for an aliphatic series of the dinitro compounds [13,14]. The curve of the ring complex for \( N = 4 \) has two waves whereas that of the linear complex shows four sigmoids. Since the linear complex composed of one O and three Rs takes two isomeric states (R–R–R–O and R–R–O–R) with different interaction energies \( (2u_{00} + u_{RO}) \) and \( u_{00} + 2u_{RO} \), respectively, the isomerization gives rise to the sigmoidal variation of \( x_0 \). In contrast, the corresponding ring complex has no isomer, and hence the potential change yields only the alteration of the redox state. Slopes \( \left( \partial x_0/\partial \zeta \right)_{\zeta=0} \) at \( \zeta = 0 \) for \( N = 3 \) and 9 demonstrate Eq. (38) well. For odd \( N \) so that \( N \geq 9 \), the ring complex behaves as the linear complex. For even \( N \), in contrast, there is still difference between the ring and the linear complex even at \( N \geq 30 \).

If the interaction were to extend to far distant redox centres, the complex might manifest an electronic band structure, as predicted from the theory of metal con-
It is obvious that $\beta \partial \zeta / \partial \beta = \zeta$. Differentiating Eq. (21) with respect to $\beta$ yields

$$\delta \chi / \delta \beta = \left[ 2 \beta u_i \exp(2 \beta u_i) \sech^2(\zeta/2) \right. + \left. (1 - \chi^2) \zeta \tanh(\zeta/2) \right] / 2 \beta \chi$$

(40)

Carrying out the differentiation of Eq. (39), we obtain the expression for the dimensionless internal energy:

$$\beta U = \beta H_j - \frac{N \zeta}{1 + e^{-\zeta}}$$

$$- \frac{\beta N \left[ (1 + \chi)^{N-1} - (1 - \chi)^{N-1} \right]}{(1 + \chi)^N + (1 - \chi)^N} \frac{\delta \chi}{\delta \beta}$$

(41)

The internal energy of an electrochemical system consists of the electrostatic energy and the chemical internal energy. In order to segregate these contributions from the $\beta U$, we estimate the dependence of the internal energy of the single mononuclear complex on the electrode potential. The partition function of the simple redox couple is given by

$$Z_1 = \exp(-\beta \mu_{oe}) + \exp(-\beta \mu_R)$$

$$= \exp(-\beta \mu_R)(1 + e^\zeta)$$

(42)

Then the dimensionless internal energy becomes

$$\beta U_1 = -\beta \partial \ln Z_1 / \partial \beta = \beta \mu_R - \zeta / (1 + e^{-\zeta})$$

(43)

If the internal energy is measured with reference $\beta \mu_R$, the potential dependence is expressed by $-\zeta / (1 + e^{-\zeta})$. As $\zeta$ increases from a sufficiently negative value, the potential-dependent term increases from 0, reaching the maximum 0.278 at $\zeta = -1.28$, and decreases along the asymptotic line $-\zeta$. Applying this variation to Eq. (41), the term $-N \zeta / (1 + e^{-\zeta})$ represents the electrostatic contribution due to the electrode reaction of the $N$ centres without interaction. Hence it is the third term that is relevant to the configurational internal energy:

$$\beta(\Delta U) = - \frac{N \left[ (1 + \chi)^{N-1} - (1 - \chi)^{N-1} \right]}{2 \chi \left[ (1 + \chi)^N + (1 - \chi)^N \right]} \times \left[ 2 \beta u_i \exp(2 \beta u_i) \sech^2(\zeta/2) \right. + \left. (1 - \chi^2) \zeta \tanh(\zeta/2) \right]$$

(44)

Fig. 3 shows variations of $\beta$(\Delta U) with $\zeta$ for several values of $\beta u_i$ at (A) $N = 10$ and (B) $N = 5$. The shape of the curve was almost independent of $N$. Since the reference of $\beta$(\Delta U) was taken as the exhaustively reduced or oxidized state, $\beta$(\Delta U) becomes zero for large values of $|\zeta|$. When $\beta u_i \geq 4$, $\beta$(\Delta U) has a V-shape with the minimum $-N \beta u_i$ for even $N$ or $-(N-1) \beta u_i$ for odd $N$ at $\zeta = 0$, as derived from Eqs. (36) and (44). Taking into account that $\mu_R(\Delta U)$ in Eq. (44) changes sign at $\zeta = 0$, we find that $(1 - \chi^2) \zeta \tanh(\zeta/2)$ is responsible for the V-shape. As a
help in understanding the V-shaped variation, the curve of \( x_0 \) vs. \( \zeta \) was drawn in the upper part of Fig. 3. The V-shape appears in the potential domain at which \( x_0 \) is retained at 1/2. According to the potential dependence of the molar fractions of isomers reported in Fig. 10 in Ref. 16, there is no isomer at \( x_0 = 1/2 \) for even \( N \). Hence the V-shape is not ascribed to the isomerization but may be due to the electrostatic energy applied to the oxidized centres for \( \zeta < 0 \) or the reduced centres for \( \zeta > 0 \). It can be expressed approximately by

\[
\beta(\Delta U) \approx [N/2]|\zeta| - N\beta u_1 \quad \text{for even } N \\
\beta(\Delta U) \approx [N/2]|\zeta| - (N - 1)\beta u_1 \quad \text{for odd } N
\]

where \([N/2]\) denotes an integral part of \( N/2 \). The slope of \([N/2]\) agrees with the number of the O or the R at \( x_0 = 1/2 \). Therefore, \([N/2]|\zeta|\) is the electrostatic contribution. In contrast, terms \(-N\beta u_1\) and \(-(N - 1)\beta u_1\) result from the configurational interaction.

3.3. Entropy

The entropy is defined by [25]

\[
S = k \ln \frac{Z_N + u}{T} - \frac{N}{1 + e^{-\zeta}} - \beta(\Delta U) \tag{48}
\]

Inserting Eqs. (20) and (41) into Eq. (47), we find that the term \( \beta H_i \) used for the reference of the potential cancels out. Then the dimensionless entropy is expressed by

\[
S/k = N \ln \left( \frac{1 + e^{\zeta}}{2} \right) + \ln \left( (1 + \chi)^N + (1 - \chi)^N \right)
\]

Fig. 4(A) shows variations of \( S/k \) with \( \zeta \) for various values of \( \beta u_1 \). As \( \beta u_1 \) increases from a sufficiently negative value, the \( S/k \) vs. curve has a peak at \( \zeta = 0 \), the peak increasing and then reaching a maximum \( N \ln 2 \) at \( \beta u_1 = 0 \). When \( \beta u_1 > 1 \), the peak for even \( N \) is separated into two, the potential difference of which is \( 2\beta u_1 \). In contrast, the peak for odd \( N \) always ap-
pears at $\xi = 0$, regardless of the value of $\beta U_1$. Peaks appear at the potential in which $x_O$ varies widely with $\xi$. This is clear when comparing curves for even $N$ (Fig. 4(A)) with those for odd $N$ (Fig. 4(B)) at $\xi = 0$ for $\beta U_1 \geq 4$.

In order to explain the relationship between the entropy and the electrode reaction, we obtain the expression for the entropy of the mononuclear complex. From $S_1 = k \ln Z_1 + U_1/\theta$ and Eq. (43), the entropy is expressed by

$$S_1/k = \ln(1 + e^{\xi}) - \frac{\xi}{1 + e^{-\xi}} \quad (49)$$

The curve of $S_1$ vs. $\xi$ has a peaked shape, similar to an ac voltammogram. It shows a maximum value of $\ln 2$. Intuitively, the 2 in the logarithm comes from the two kinds of species. Rewriting $\xi$ as $p$ and $q$ by use of Eq. (22), we have

$$S_1/k = -p \ln p - q \ln q$$

This is an equation for the mixing entropy of ideal two components [26]. From the comparison of Eqs. (48) and (49), the mixing entropy of the $N$-nuclear complex is predicted to be $N \ln 2$, but was evaluated to be $0.69N \ln 2$ for $\beta U_1 \geq 4$. This is probably equal to $N(\ln 2)^2$. The value can be explained by the duplicated alternative states: either the $O$ or the $R$, and either a hetero pair (R-O) or a homo pair (R-R or O-O).

Two kinds of entropy may be defined: the configurational entropy, $S_{\text{conf}}$, which is ascribed to the number of the configurational arrangement of isomers with a given redox state; and the redox entropy, which results from the O and the R. Since the former is included partly by the latter, it may be separated only when $x_O$ is invariant to $\xi$ or only when the redox entropy is ignored. Thus the configurational entropy is specific in the potential domains $|\xi| < \beta U_1$ at even $N$ and $5 < |\xi| < \beta U_1 + 2$ at odd $N$, e.g. $|\xi| < 8$ at $\beta U_1 = 8$ in Fig. 4(A) and $5 < |\xi| < 10$ at $\beta U_1 = 8$ in Fig. 4(B). The number of the configurational isomers given by $n_c = \exp(S_{\text{conf}}/k)$ was evaluated for various values of $N$. The value of $n_c$ was 2 for even $N$, whereas it was $N$ for odd $N$ (see Fig. 4). The two or $N$ isomers correspond to the rotational symmetry [13]. The peak in the potential domain $|\xi| < 5$ in Fig. 4(B) may include the redox entropy because the one-electron charge-transfer reaction occurs in this domain. Since the one-electron transfer reaction generates $\ln 2$ entropy, the peak height at $\xi = 0$ is expected to be $\ln N + \ln 2$. This agrees with the height at $\xi = 0$ in Fig. 4(B).

4. Conclusion

The electrochemically significant partition function of a polynuclear complex is a product of the canonical partition function and the Boltzmann factor of an arbitrary reference species. It is a function of the electrode potential, the interaction energy and the number of redox centres. The partition function derived by the eigenvalue technique agrees with the generating function based on the local equilibrium probabilities in so far as it concerns isomeric configuration. This may be generalized to the prediction that a product and a summation of the Fermi distribution under the microscopic equilibrium condition yield the statistical thermodynamic function $\Phi(N)$ equivalent to the partition function. The $\Phi(N)$ allowed us to evaluate the molar fraction of the oxidized centres, the internal energy and the entropy.

The potential dependence of the internal energy and the entropy is useful for discussing the redox states and the configurational states. The internal energy is a measure of the redox state rather than the configurational states. In the potential domain at which $x_O = 1/4$, the entropy increases by $N(\ln 2)^2$, which results from the mixing entropy of the R and the O as well as the mixing entropy of the R-O and the R-R (O-O). In the other potential domain, the entropy is expressed by a simple sum of the configurational and the redox contribution.

References