

sion between the relatively large electronic charge and bond pairs at the β -carbon. The MNDO results are consistent with the TS where C α -O bond polarization is the rate-determining step, which follows the pre-equilibrium involving the acidic hydrogen shift towards the carbonyl oxygen.

Acknowledgement. We thank the Ministry of Education and the Korea Center for Theoretical Physics and Chemistry for support of this work.

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A Nonlinear Theory of Diffusion-Driven Instability in the Oregonator

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A nonlinear theory presented previously is applied to the Oregonator, which is a model for the Belousov-Zhabotinskii reaction, to study instability near the critical point driven by diffusions. The result shows that the theory may be applied to an actual system.

Introduction

Theoretical and experimental studies of instability in chemically reacting systems date back at least to the early part of this century.^{1,2} Lotka¹ proposed in 1920 a simple model of autocatalytic chemical reactions which shows sustained oscillations in the concentration of the autocatalytic species when open to a flow of matter through the system. Bray² discovered this kind of sustained oscillation in an inorganic redox reaction. In 1952 Turing³ showed that stable spatial patterns can be obtained when chemical reactions are coupled to the process of diffusion. Thus, he laid the foundation for a biochemical theory of morphogenesis. Much attention has been given to that subject in the past 20 years since the dramatic phenomena in the Belousov-Zhabotinskii (B-Z) reaction sparked the interest of experimentalists and

theoreticians in chemistry and other fields.^{4,7}

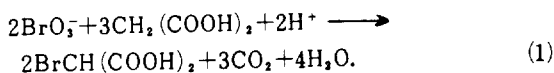
Recently Lee and his coworkers⁸ have proposed a nonlinear theory for the fluctuations of intermediates in the Brusselator near the critical point caused by diffusion. The method used⁹⁻¹² is the two time scaling method which is one of the most widely used methods. In the conventional two time scaling method the whole range of time is divided into three regions of time. The initial region of time is the range of time where the linear approximation is valid. The second region is the region in which the nonlinear effect becomes important and the system approaches a steady state (or equilibrium state). The two time scaling method used⁸ is different from the conventional method in the sense that a slight nonlinear effect is included in the initial time region where the linear approximation is valid. Their nonlinear theory shows that fluctuations close to the critical point approach

the value of a stable steady state or deviate infinitely from an unstable steady state, as time goes to infinity, while the linear theory gives approximately time-independent fluctuations.

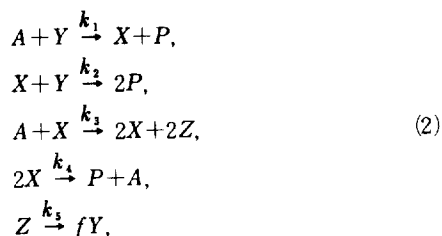
The purpose of the present paper is to investigate that the nonlinear theory⁸ is applicable to the actual reacting system with the aid of the Oregonator.^{6,7} We first discuss the linear case for the Oregonator far from the steady state. Then, the nonlinear case is discussed with the aid of the two time scaling method.

Theory

The overall B-Z reaction is^{4,7}



Field, Körös and Noyes proposed a complex system of 10 chemical reactions with 7 intermediates as a model for the B-Z reaction. From this system Field and Noyes⁷ extracted a simpler model that appears to retain the most important features of the Field-Körös-Noyes (FKN) mechanism. Their simplification, called the Oregonator, is given by



where A is the reactant, P is the product and X, Y, and Z are the concentrations of the intermediates HBrO_2 , Br^- and Ce(IV) , respectively, f is a stoichiometric factor. Taking $[A] \approx 0.06\text{M}$, the rate constants are given as⁷

$$\begin{aligned} k_1 &\approx 2.1\text{M}^{-1}\text{S}^{-1}, \quad k_2 \approx 2 \times 10^9\text{M}^{-1}\text{S}^{-1}, \quad k_3 \approx 10^4\text{M}^{-1}\text{S}^{-1} \\ k_4 &\approx 4 \times 10^7\text{M}^{-1}\text{S}^{-1}, \quad k_5 \approx 0.4[\text{BrCH}(\text{COOH})_2]\text{S}^{-1}. \end{aligned} \quad (3)$$

Since the concentration of the reactant is held constant, the stoichiometric factor f and the rate constant k_5 are controllable variables. The behavior of the Oregonator depends critically on the values of f and k_5 .⁷

Including the diffusions of the intermediates, the rate equations are

$$\begin{aligned} \frac{\partial}{\partial t} X &= D_x \nabla^2 X + k_1 AY - k_2 XY + k_3 AX - 2k_4 X^2, \\ \frac{\partial}{\partial t} Y &= D_y \nabla^2 Y - k_1 AY - k_2 XY + f k_5 Z, \\ \frac{\partial}{\partial t} Z &= D_z \nabla^2 Z + 2k_3 AY - k_5 Z, \end{aligned} \quad (4)$$

where D_x , D_y , and D_z are the diffusion coefficients of the intermediates X, Y, and Z, respectively. In order to simplify above differential equations, let us introduce the following transformation for the variables

$$\begin{aligned} x &= \frac{k_2}{k_1 A} X \approx 1.6 \times 10^{10} [\text{HBrO}_2], \quad y = \frac{k_2}{k_1 A} Y \approx 3.3 \times 10^6 [\text{Br}^-] \\ z &= \frac{k_2 k_5}{2k_1 k_3 A^2} Z \approx 1.3 \times 10^7 [\text{Ce(IV)}], \quad \xi = \frac{k_1}{k_3} \approx 2 \times 10^{-4}, \end{aligned}$$

$$\tau = (k_1 A) t = 0.13t$$

$$p = \frac{k_1 A}{k_3} \approx \frac{0.126}{k_3}, \quad q = \frac{2k_1 k_4}{k_2 k_3} \approx 8.4 \times 10^{-6}, \quad (5)$$

$$\nabla'^2 = \frac{D_x}{k_3} \nabla^2, \quad \eta^2 = \frac{D_y k_5}{D_z k_1 A} \approx 8.9 \frac{D_y}{D_z} k_3,$$

$$\eta'^2 = \frac{D_x}{D_z} \frac{k_5}{k_3 A} \approx 1.7 \times 10^{-3} \frac{D_x}{D_z} k_3.$$

With the aid of the scaled variables, the rate equations are

$$\begin{aligned} \xi \frac{\partial}{\partial \tau} x &= \eta'^2 \nabla'^2 x + y - xy + x - 2qx^2, \\ \frac{\partial}{\partial \tau} y &= \eta^2 \nabla'^2 y - y - xy + 2fz, \\ p \frac{\partial}{\partial \tau} z &= \nabla'^2 z + x - z. \end{aligned} \quad (6)$$

The value of ξ is very small and so is η'^2 since the magnitude of k_5 is less than unity.⁷ Therefore, eq. (6) can be reduced to the following system involving only two intermediates, that is,

$$\begin{aligned} \frac{\partial}{\partial \tau} y &= \eta^2 \nabla'^2 y - y - g(y)y + 2fz, \\ p \frac{\partial}{\partial \tau} z &= \nabla'^2 z + g(y) - z, \end{aligned} \quad (7)$$

where

$$x = g(y) = \{1 - y + [(y-1)^2 + 8qy]^{1/2}\} / 4q$$

From now on we shall omit the superscript prime in the Laplacian operator. Let x_0 , y_0 , and z_0 be the values of the homogeneous steady state. Expansion in terms of $u_1 = y - y_0$ and $u_2 = z - z_0$ leads to

$$\begin{aligned} \frac{\partial}{\partial \tau} u_1 &= (\eta^2 \nabla^2 - 1 - g - y_0 g') u_1 + 2f u_2 - (g' + y_0 g'') u_1^2 \\ &\quad - (g'' + y_0 g''') u_1^3 + \dots, \\ p \frac{\partial}{\partial \tau} u_2 &= g' u_1 + (\nabla^2 - 1) u_2 + g'' u_1^2 + g''' u_1^3 + \dots, \\ g^{(n)} &= \frac{1}{n!} \frac{d^n}{dy^n} g|_{y=y_0}. \end{aligned} \quad (8)$$

At first let us consider the linear case of eq. (8).

(A) Linear case

Neglecting the nonlinear terms in eq. (8), the linear equation is

$$\begin{aligned} \frac{\partial}{\partial \tau} u &= M u \\ u &= (u_1, u_2)^T, \quad M = \begin{pmatrix} \eta^2 \nabla^2 - 1 - g - y_0 g' & 2f \\ g' / p & (\nabla^2 - 1) / p \end{pmatrix} \end{aligned} \quad (9)$$

The linear stability conditions for the homogeneous case are

$$\begin{aligned} \det M &= 1 + g + y_0 g' - 2fg' > 0, \\ \text{tr } M &= -(1 + g + y_0 g' + p^{-1}) < 0. \end{aligned} \quad (10)$$

Figures 1 and 2 show the regions of stability and instability between y_0 and f, and y_0 and p, respectively. As shown in Figure 1, there are the stable and unstable regions in the case that y_0 is between about 0.6 and 1.6, depending on f.

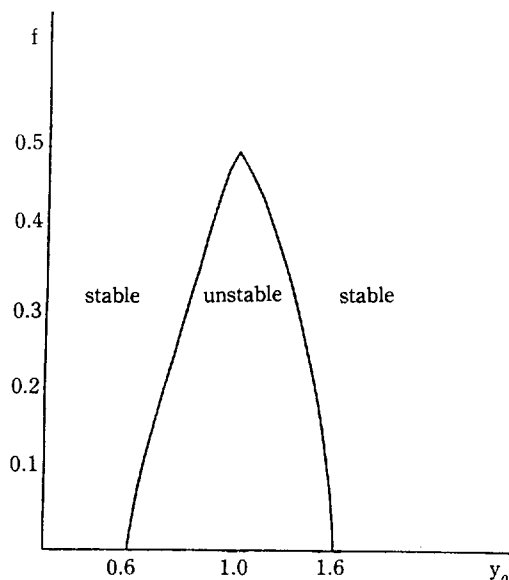


Figure 1. The diagram of linear stability between y_0 and f .

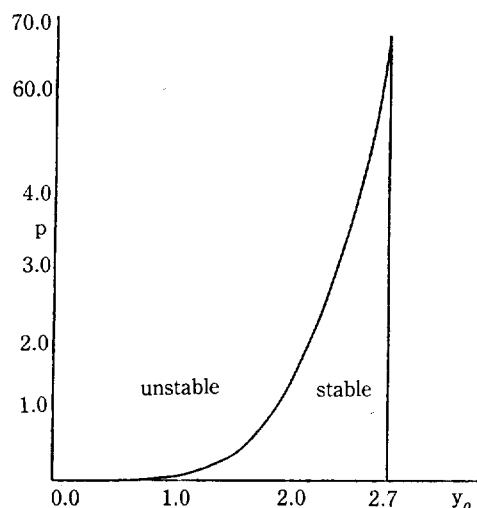


Figure 2. The linear stability diagram between y_0 and p .

When y_0 is less than 1.0, p should be extremely small so that the system is stable. This case is physically unrealistic. In fact, Field and Noyes⁷ estimated that $k_5 \approx 1$, i.e., $p \approx 0.126$. Taking $p \approx 0.126$, the system is stable, if $1.4 \leq y_0 \leq 1.7$. Let us assume that the system is somewhere in the stable region. Then, when the system becomes inhomogeneous, the intermediates are diffused. The diffusions will drive the system to a new state, whether it is stable or unstable. Since it is more interesting to study the transition from the stable state to the unstable one, we shall consider the effect of diffusions on such transition.

To discuss the diffusion-driven instability linearly, let us take one dimensional diffusion for simplicity, that is,

$$u(x, \tau) = u(\tau) \cos kx. \quad (11)$$

Then, we have

$$\frac{d}{d\tau} u(\tau) = M_{n,k} u(\tau); M_{n,k} = \begin{pmatrix} -(\eta^2 k^2 + 1 + g + y_0 g'), & 2f \\ g'/p, & -(1+k^2)/p \end{pmatrix} \quad (12)$$

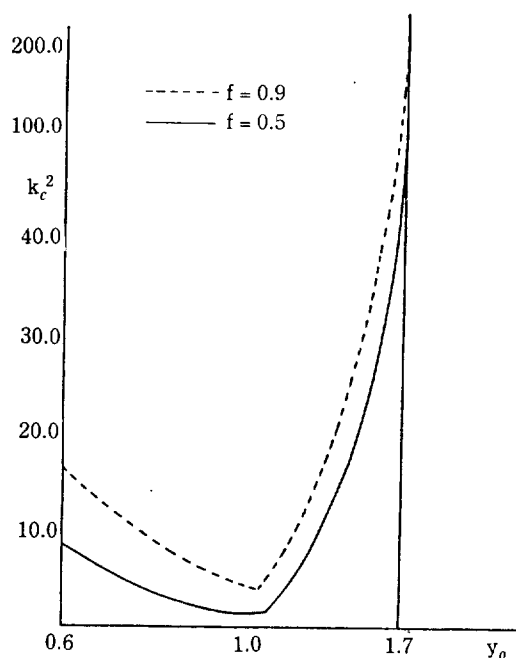


Figure 3. The relation between y_0 and k_c^2 .

If $\det M_{n,k}$ is positive, the system is still stable. When $M_{n,k} < 0$, the diffusions drive the system to an unstable state. The variables η^2 and k^2 at the critical point are

$$\eta_c^2 = \frac{[2fg'(2fg' - 1 - g - y_0 g')]^{1/2}}{k_c^2(1+k_c^2)}, \quad (13)$$

$$k_c^2 = \frac{2fg' - 1 - g - y_0 g' - [2fg'(2fg' - 1 - g - y_0 g')]^{1/2}}{1 + g + y_0 g'}.$$

The value of k_c^2 is only positive for $0.5 \leq f$ when $0.6 \leq y_0 \leq 1.7$, as shown in Figure 3, while η_c^2 is positive in any value of y_0 . This means that the transition can occur only in that region.

In order to analyze the dynamic behavior of the system we have to obtain the eigenvalues of eq. (12). When one of the eigenvalues is positive, the fluctuations become divergent, as time goes to infinity. The system, however, approaches the stable state, if the eigenvalues are negative. Let us consider the dynamic behavior of eq. (12) extremely close to the critical point. The eigenvalues of the matrix and their corresponding eigenvectors near the critical point are

$$\lambda_1 = -\frac{[(1+k_c^2)^2 + 2pf g']}{p(1+k_c^2)} + O(\eta - \eta_c),$$

$$\lambda_2 = -\frac{2\eta_c k_c^2 (1+k_c^2)^2}{(1+k_c^2)^2 + 2pf g'} (\eta - \eta_c) + O(\eta - \eta_c)^2,$$

$$\Psi^1 = (\Psi_1^1, \Psi_2^1)^T = \left(-\frac{2pf}{1+k_c^2}, 1\right)^T, \quad (14)$$

$$\Psi^2 = (\Psi_1^2, \Psi_2^2)^T = \left(\frac{1+k_c^2}{g'}, 1\right)^T,$$

$$\bar{\Psi}^1 = (\bar{\Psi}_1^1, \bar{\Psi}_2^1)^T = \frac{(1+k_c^2)^2}{(1+k_c^2)^2 + 2pf g'} \left(-\frac{g'}{1+k_c^2}, 1\right),$$

$$\bar{\Psi}^2 = (\bar{\Psi}_1^2, \bar{\Psi}_2^2)^T = \frac{2pf g'}{(1+k_c^2)^2 + 2pf g'} \left(\frac{1+k_c^2}{2pf}, 1\right),$$

where Ψ^a and $\bar{\Psi}^a$ are the right and left eigenvectors corresponding to λ_a , respectively. It can be easily checked that the eigenvectors satisfy the orthonormal conditions.⁸ The eigenvalue λ_1 is negative in the region that $1.4 \leq y_0 \leq 1.6$, where the theory⁸ holds. In that region, very close to the critical point, the solution is

$$u(x, \tau) \cong A \Psi^2 \cos k_c x. \quad (15)$$

The above result shows that fluctuations are time-independent near the critical point, which does not describe the actual phenomena properly. Thus, in the next section we shall consider the nonlinear equation given in eq. (8).

(B) Nonlinear case

We shall use the two time scaling method already discussed⁸ to investigate nonlinear stability for the Oregonator. The scaled times and vectors are⁸

$$\begin{aligned} \tau_m &= \varepsilon^{2m} \tau, \quad m=0, 1, \\ u_j &= \sum_i \varepsilon^i u_{ij}, \quad i, j=1, 2, \end{aligned} \quad (16)$$

Where τ_0 is the region of time where not only the linear approximation is valid but also a slight nonlinear effect is included and τ_1 is the region of time in which the nonlinear effect becomes important. The parameter ε has been defined as

$$\varepsilon^2 = |\eta - \eta_c|. \quad (17)$$

Assuming that the fluctuations depend on τ_0 and τ_1 through the amplitude of fluctuations A , that is,

$$u(x, \tau_0, \tau_1) = A(\tau_0, \tau_1) \Psi^2 \cos k_c x, \quad (18)$$

the following equations in the initial region of time, τ_0 are obtained

$$\frac{\partial}{\partial \tau_0} (u_{11}, u_{12})^T = M_{\eta_c, \kappa_c} (u_{11}, u_{12})^T, \quad (19a)$$

$$\frac{\partial}{\partial \tau_0} (u_{21}, u_{22})^T = M_{\eta_c, \kappa_c} (u_{21}, u_{22})^T - u_{11}^2 (g' + y_0 g'', -g''/p)^T. \quad (19b)$$

Eq. (19a) is just the linear equation already discussed. Thus, A is approximately independent of τ_0 near the critical point. Following the procedure given in ref. 8, we have the asymptotic solution in the initial region of time as follows

$$(u_{11}, u_{12})^T \cong A \varepsilon \Psi^2 \cos k_c x - \frac{1}{2} A^2 \varepsilon^2 (\Psi_1^2 (\phi^1 + \phi^2 \cos 2k_c x)), \quad (20)$$

where

$$\begin{aligned} \phi^1 &= (\phi_1^1, \phi_1^2)^T = \frac{1}{H} [g' + y_0 g'' - 2fg'', -g''(1+g+y_0 g') \\ &\quad + g'(g' + y_0 g'')]^T, \end{aligned}$$

$$\begin{aligned} \phi^2 &= \frac{1}{R} [(1+4k_c^2) (g' + y_0 g'') - 2fg'', \\ &\quad -g''(4\eta_c^2 k_c^2 + 1+g+y_0 g') + g'(g' + y_0 g'')]^T, \end{aligned}$$

$$H = 1+g+y_0 g' - 2fg'$$

$$R = (4\eta_c^2 k_c^2 + 1+g+y_0 g') (1+4k_c^2) - 2fg'.$$

Using eq. (17), λ_2 is defined as

$$\lambda_2 = -\gamma \varepsilon^2; \gamma = \frac{2\eta_c k_c^2 (1+k_c^2)^2}{(1+k_c^2)^2 + 2pf g'}, \quad \text{sign } \gamma = \text{sign } (\eta - \eta_c). \quad (22)$$

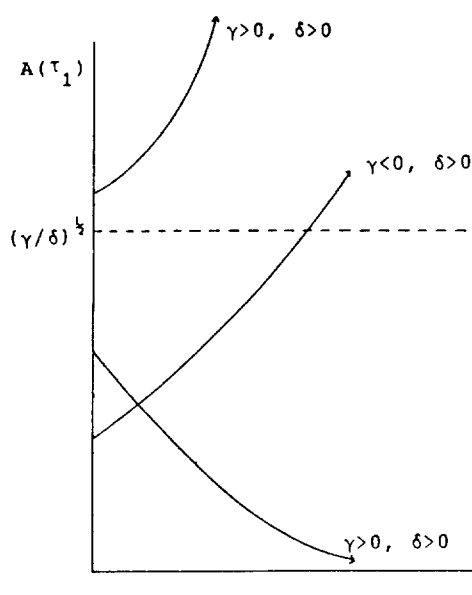


Figure 4. The dependence of $A(\tau_1)$ on time τ_1 .

Substituting eqs. (20) and (22) into eq. (8), taking terms up to the third order in ε and using the orthonormalization condition given in eq.(2.13) of ref. 8, we have

$$\frac{d}{d\tau_1} A = -\gamma A + \delta A^3, \quad (23)$$

where

$$\begin{aligned} \delta &= \frac{(1+k_c^2)^3}{g'^2 [(1+k_c^2)^2 + 4pf g']} \{ [(1+k_c^2) (g' + y_0 g'') - 2fg''] \\ &\quad \times (\phi_1^1 + \frac{1}{2} \phi_1^2) - \frac{3}{4} [(1+k_c^2) (g'' + y_0 g''') - 2fg'''] \}. \end{aligned} \quad (24)$$

δ is positive for $f \geq 0.5$ in the region of $1.4 \leq y_0 \leq 1.6$. When η is larger than η_c , $A = 0$ is stable and $\pm (r/\delta)^{1/2}$ are unstable. The amplitude becomes zero as $\tau_1 \rightarrow \infty$, if the initial state is between $-(r/\delta)^{1/2}$ and $(r/\delta)^{1/2}$. Otherwise, A becomes divergent. In the case that $\eta < \eta_c$, there is only a state which is unstable, that is, $A = 0$. Thus, A diverges as $\tau_1 \rightarrow \infty$. The dependence of the amplitude of fluctuations on τ_1 is shown in Figure 4.

Conclusion and Discussion

We have applied the nonlinear theory⁸ to the reduced Oregonator, which is a model for the B-Z reaction. The result shows that the theory may be applied to an actual system, if there are available data. It should be mentioned that in the result the region of y_0 , $1.4 \leq y_0 \leq 1.6$, where the theory is valid, is approximate, since the data used have been roughly estimated.⁷ There are, however, some other points to be pointed out.

(1) Since there are some problems in the data for the Oregonator, that is, q is too small and k_5 is too large, the present result should be compared with other models.¹³

(2) We have reduced the original Oregonator to the second order system. Thus, it is necessary to extend the theory to the third order system to study the diffusion-driven instability more precisely.

(3) Finally, in eq. (23) there are cases that the amplitude of

fluctuations is divergent, since we have considered the nonlinear terms up to the third order in ϵ . The higher order terms should be included, if necessary.

Acknowledgement. This work was supported by a grant from the Basic Science Research Institute Program, Ministry of Education of Korea, 1986. We are also grateful to Mr. Seokmin Shin for helpful discussions.

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13. Comparison of the present result with other models will be given in detail in a forthcoming paper.

Cross Interaction Between Identical Groups

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Various useful relations involving Hammett's and Brønsted's coefficients are derived for cross interactions between identical groups: $\rho_{ii} = \rho^N + \rho^L$, $\rho^L - \rho^N = 1$, $\beta_{ii} = \beta_N + \beta_L$ and $\beta_N - \beta_L = 1$. The use of these relations enable us to correctly interpret the transition state structure. Another advantage of the use of these relations is to use ρ/ρ_e for the determination of corresponding β values instead of plotting $\log k$ vs pK_{lg} , once ρ_e values for standardizing equilibria are obtained.

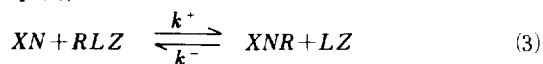
Cross interaction between two substituents has become a useful concept in the study of reaction mechanisms.¹ Multiple linear regression analysis² involving experimental rate constants k_{XZ} together with σ_X and σ_Z values provides us with the cross interaction constant ρ_{XZ} for the interaction between two substituents X and Z in accordance with eq.(1)³.

$$\log(k_{XZ}/k_{HH}) = \rho_X \sigma_X + \rho_Z \sigma_Z + \rho_{XZ} \sigma_X \sigma_Z \quad (1)$$

Replacing one of the substituents by H, e.g. Z = H, in eq. (1) reverts to the simple Hammett equation(2); the ρ_X and ρ_Z values in eq. (1) should therefore be more rigorously represented as ρ_{XH} and ρ_{HZ} .

$$\log(k_X/k_H) = \rho_X \sigma_X \quad (2)$$

Let us consider a reversible nucleophilic substitution (S_N) reaction, eq. (3),



where XN and LZ represent a nucleophile with a substituent X and a leaving group with a substituent Z, respectively.

The ρ_X and ρ_Z in eq. (1) now becomes the reaction constants for substituent variations in the nucleophile and leaving group. For an identity S_N reaction, i.e., XN = LZ,

$$\log(k_{ii}/k_{HH}) = (\rho^N + \rho^L) \sigma_i + \rho_{ii} \sigma_i^2 \quad (4)$$

where $\rho^N = \rho_{iH}$ and $\rho^L = \rho_{Hi}$; Obviously $\rho^N \neq \rho^L$ in general.

Hereafter, we adopt a convention that ρ^+ (for k^+) = ρ^L and ρ^- (for k^-) = ρ^N . It has been shown that the neglect of second order term in the Marcus equation leads to⁽⁴⁾

$$\rho^+ + \rho^- = \rho_{ii} \quad \text{i.e.,} \quad \rho^L + \rho^N = \rho_{ii} \quad (5)$$

$$\text{Thus,} \quad \log(k_{ii}/k_{HH}) = \rho_{ii} (\sigma_i + \sigma_i^2) \quad (6)$$

To be consistent with the approximations adopted in the derivation of eq. (1)³, we neglect the term in σ_i^2 , which simplifies eq. (6) to

$$\log(k_{ii}/k_{HH}) = \rho_{ii} \sigma_i \quad (7)$$

$$\text{Since} \quad K_{ii} = k_{ii}/k_{iH} = k^+/k^-, \quad (K_{ii} = K_{iH}^{-1}) \quad (8)$$

$$\rho_e = \rho^+ - \rho^-, \quad \text{i.e.,} \quad \rho_e = \rho^L - \rho^N \quad (9)$$

where ρ_e is the Hammett's coefficient for the equilibrium constant K_{Hi} ⁵, and $\rho^+ = \rho^L = \rho_{Hi}$ and $\rho^- = \rho^N = \rho_{iH}$. Eqs. (5) and (9) constitute a set of fundamental relations for the identity exchange reactions.

Definition of Brønsted's coefficient β leads us to more useful correlations for the identity reactions.⁶

$$\beta_L = \frac{d \log k}{d pK} = \frac{d \log k^+}{d \sigma} / \frac{d pK}{d \sigma} = \frac{\rho^+}{\rho_e} = - \frac{\rho^L}{\rho_e} \quad (10a)$$

Likewise,