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Specification of the Adsorption Model in Hydroxyapatite Chromatography. II. The Case of a Multicomponent System

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Abstract

The earlier argument for the grand canonical single component system is extended to the general case of a multicomponent system. The adsorption isotherms for the respective components of the mixture are calculated; these are dependent on one another.

INTRODUCTION

The purpose of this paper is to extend the earlier argument for a single component adsorbed system (*1*) to the general case of a multicomponent system, and to lay a foundation for the competition chromatographic model which will be discussed in a later paper (*2*). The present argument is based upon Assumptions 1-7 in Theoretical Section (A) of the preceding paper (*1*).

THEORETICAL

(A) Adsorption Isotherms for a Multicomponent System

The partition function, Ξ, for the grand canonical multicomponent adsorbed system fulfilling the Assumptions 1-7 in Theoretical Section (A) of Ref. *1* can be written as

$$\Xi = \sum_{\sum_{\rho'=1}^{\rho} n'_{(\rho')} \leqslant M} e^{\frac{1}{kT}\sum_{\rho'=1}^{\rho} n'_{(\rho')}\mu_{(\rho')}} Z \tag{1}$$

where

$$Z = \omega(\boldsymbol{\theta}')e^{-U'(\boldsymbol{\theta}')/kT} \sum_{\{\{j\}\}_{\boldsymbol{\theta}'}} e^{-U_{\{\{j\}\}_{\boldsymbol{\theta}'}}/kT} \prod_{\rho'=1}^{\rho} [v_{(\rho')}(\boldsymbol{\theta}')]^{n'_{(\rho')}} \tag{2}$$

$$\boldsymbol{\theta}' = (\theta'_{(1)}, \theta'_{(2)}, \ldots, \theta'_{(\rho)}) \tag{3}$$

and

$$\theta'_{(\rho')} = \frac{x'_{(\rho')} n'_{(\rho')}}{n_0} \qquad (\rho' = 1, 2, \ldots, \rho) \tag{4}$$

The physical meanings of the symbols involved in Eqs. (1)–(4) are:

ρ' = a molecular component of the mixture; ρ' represents one of the components $1, 2, \ldots, \rho$.
$n'_{(\rho')}$ = total number of the molecules of component ρ' on the adsorbent surface under consideration varying between 0 and M.
M = upper limit of the $\Sigma_{\rho'=1}^{\rho} n'_{(\rho')}$ value; this depends upon the ratios among $n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho)}$, and the type of the adsorbed phase.
$\mu_{(\rho')}$ = chemical potential for molecular component ρ'.
k = Boltzmann constant.
T = absolute temperature.
$x'_{(\rho')}$ = average number of adsorbing site(s) occupied by a molecule of component ρ' when it is adsorbed. Here, the physical meaning of "occupying" is not specified. Cf. the explanation of the parameter x' in the preceding paper (*1*).
n_0 = total number of the adsorbing sites on the adsorbent surface.
$\theta'_{(\rho')}$ = surface molecular density for component ρ' on the adsorbent.
$\omega(\boldsymbol{\theta}')$ = total number of the microscopical states concerning

both location and orientation of all the molecules on the adsorbent surface, occurring when the molecular densities of the respective components of the mixture are $\theta'_{(1)}, \theta'_{(2)}, \ldots, \theta'_{(\rho)}$.

$U'(\boldsymbol{\theta}')$ = total mutual interaction energy among all the molecules on the adsorbent surface occurring when the surface molecular densities of the respective components of the mixture are $\theta'_{(1)}, \theta'_{(2)}, \ldots, \theta'_{(\rho)}$.

$\{\{\mathbf{j}\}\}_{\boldsymbol{\theta}'}$ = a microscopical state concerning configuration of all the molecules on the adsorbent surface, occurring when the surface molecular densities of the respective components of the mixture are $\theta'_{(1)}, \theta'_{(2)}, \ldots, \theta'_{(\rho)}$. For detail, see both Eqs. (11) and (12).

$\prod_{\rho'=1}^{\rho} [\dot{\nu}_{(\rho')}(\boldsymbol{\theta})]^{n'_{(\rho')}}$ = total number of the microscopical states concerning configuration of all the molecules on the adsorbent surface, occurring when the surface molecular densities of the respective components of the mixture are $\theta'_{(1)}, \theta'_{(2)}, \ldots, \theta'_{(\rho)}$. For detail, see the explanation of Eq. (13).

$U_{\{\{\mathbf{j}\}\}_{\boldsymbol{\theta}'}}$ = total interaction energy of all the molecules with adsorbing sites on the adsorbent surface occurring when a microscopical state $\{\{\mathbf{j}\}\}_{\boldsymbol{\theta}'}$ is realized.

$\omega(\boldsymbol{\theta}')$ can be represented as

$$\omega(\boldsymbol{\theta}') = \omega[\mathbf{n}'] = \frac{1}{\prod_{\rho'=1}^{\rho} n'_{(\rho')}!} \prod_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\phi_{(\rho'')}[\mathbf{n}'']\}_I \tag{5}$$

where

$$\mathbf{n}' = (n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho)}) \tag{6}$$

and if ω is considered to be a function of $\mathbf{n}'$ instead of $\boldsymbol{\theta}'$, brackets are used instead of parentheses to insert the variables; similar expressions will also be applied to other parameters. In the right-hand side of Eq. (5), ρ'' varies arbitrarily between 1 and ρ with an increase of I (cf. Appendix I), and $\phi_{(\rho'')}[\mathbf{n}'']$ represents the increment in times of the total number of both location and orientation of all the molecules on the adsorbent surface

occurring when the $n''_{(\rho'')}$th molecule of component ρ'' is added; it is assumed that $n''_{(\rho'')} - 1$ molecules of component ρ'' and $n''_{(1)}, n''_{(2)}, \ldots, n''_{(\rho''-1)}, n''_{(\rho''+1)}, \ldots, n''_{(\rho)}$ molecules of the other components existed on the adsorbent surface before the addition, and that the molecules of any component are provisionally discernible from one another among them. $\{\phi_{(\rho'')}\}_{I=1}$ or $\phi_{(\rho'')}[0, \ldots, 0, 1, 0, \ldots, 0]$ represents, however, the number of both location and orientation of a molecule of component ρ'' on the adsorbent surface occurring in the absence of any other molecules; this can be written as

$$\phi_{(\rho'')}[0, \ldots, 0, 1, 0, \ldots, 0] = n_0 z \tag{7}$$

in which z represents the coordination number of the adsorbing sites on the adsorbent surface.

Let us introduce the parameter

$$p_{(\rho'')}(\boldsymbol{\theta}'') = p_{(\rho'')}[\mathbf{n}''] = \frac{\phi_{(\rho'')}[\mathbf{n}'']}{\phi_{(\rho'')}[0, \ldots, 0, 1, 0, \ldots, 0]} \tag{8}$$

By its definition, $p_{(\rho'')}$ can be assumed to fulfill the relationships

$$\left.\begin{aligned} &\lim_{\sum_{\rho'=1}^{\rho} \theta''_{(\rho')} \to 0} p_{(\rho'')}(\boldsymbol{\theta}'') \approx \lim_{\sum_{\rho'=1}^{\rho} n''_{(\rho')} \to 1} p_{(\rho'')}[\mathbf{n}''] = 1 \\ &\text{and} \\ &\lim_{\sum_{\rho'=1}^{\rho} \theta''_{(\rho')} \to \left[\sum_{\rho'=1}^{\rho} \theta''_{(\rho')}\right]_{\max}} p_{(\rho'')}(\boldsymbol{\theta}'') \approx \lim_{\sum_{\rho'=1}^{\rho} n''_{(\rho')} \to M+1} p_{(\rho'')}[\mathbf{n}''] = 0 \end{aligned}\right\} \tag{9}$$

and, in many instances, to decrease with an increase of $\Sigma_{\rho'=1}^{\rho} \theta''_{(\rho')}$ or $\Sigma_{\rho'=1}^{\rho} n''_{(\rho')}$. Similarly to the case of a single component system, $p_{(\rho'')}$ represents a probability provided the adsorption configuration of a molecule is independent of $\boldsymbol{\theta}''$ or $\mathbf{n}''$ (see Ref. *1*).

By using Eqs. (7) and (8), and again introducing the new parameter

$$\{y_{(\rho'')}[\mathbf{n}'']\}_I = \frac{\{p_{(\rho'')}[\mathbf{n}'']\}_I}{1 - \dfrac{I-1}{M}} \tag{10}$$

Eq. (5) can be rewritten as

$$\omega(\boldsymbol{\theta}') = \omega[\mathbf{n}'] = \frac{(n_0 z)^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}}}{\prod_{\rho'=1}^{\rho} n'_{(\rho')}!} \prod_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{p_{(\rho'')}[\mathbf{n}'']\}_I$$

$$= \left(\frac{n_0 z}{M}\right)^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \frac{M!}{\prod_{\rho'=1}^{\rho} n'_{(\rho')}! \left(M - \sum_{\rho'=1}^{\rho} n'_{(\rho')}\right)!} \prod_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{y_{(\rho'')}[\mathbf{n}'']\}_I \quad (5')$$

In Appendix I, a remark on both Eqs. (5) and (5′) is made.

Below is argued the third term in the right-hand side of Eq. (2). Thus, in the term, $\{\{\mathbf{j}\}\}_{\boldsymbol{\theta}'}$ is defined as

$$\{\{\mathbf{j}\}\}_{\boldsymbol{\theta}'} \equiv \{\{\mathbf{j}_{(1)}\}, \{\mathbf{j}_{(2)}\}, \ldots, \{\mathbf{j}_{(\rho')}\}, \ldots, \{\mathbf{j}_{(\rho)}\}\} \quad (11)$$

in which $\{\mathbf{j}_{(\rho')}\}$ is defined as

$$\{\mathbf{j}_{(\rho')}\} \equiv \{j_{(\rho'),1}, j_{(\rho'),2}, \ldots, j_{(\rho'),i}, \ldots, j_{(\rho'),n'_{(\rho')}}\} \quad (12)$$

In Eq. (12), i ($i = 1, 2, \ldots, n'_{(\rho')}$; $\rho' = 1, 2, \ldots, \rho$) represents the number provisionally given to each of the $n'_{(\rho')}$ molecules of component ρ' on the adsorbent surface; $j_{(\rho'),i}$ where

$$j_{(\rho'),i} = 1, 2, \ldots, \dot{\nu}_{(\rho')}(\theta') \quad (13)$$

represents the number given to each of the configurations which the ith molecule of component ρ' can take provided the surface molecular densities of the respective components of the mixture are $\theta'_{(1)}, \theta'_{(2)}, \ldots, \theta'_{(\rho)}$. The maximum value, $\dot{\nu}_{(\rho')}(\boldsymbol{\theta}')$, of $j_{(\rho'),i}$ or the total number of the possible configurations of a molecule of component ρ' is independent of i. This means that the total number of the microscopical states $\{\{\mathbf{j}\}\}_{\boldsymbol{\theta}'}$ is equal to $\Pi_{\rho'=1}^{\rho} [\dot{\nu}_{(\rho')}(\boldsymbol{\theta}')]^{n'_{(\rho')}}$. It can be assumed that

$$\lim_{\sum_{\rho''=1}^{\rho} \theta'_{(\rho'')} \to 0} \dot{\nu}_{(\rho')}(\boldsymbol{\theta}') \approx \lim_{\sum_{\rho''=1}^{\rho} n'_{(\rho'')} \to 1} \dot{\nu}_{(\rho')}[\mathbf{n}'] = \nu_{(\rho')} \quad (14)$$

where $\nu_{(\rho')}$ is a constant greater than, or equal to, unity; in many instances,

$\dot{\nu}_{(\rho')}$ would decrease with an increase of $\Sigma_{\rho''=1}^{\rho} \theta'_{(\rho'')}$ or $\Sigma_{\rho''=1}^{\rho} n'_{(\rho'')}$ sterically hindered by geometrical interactions with other molecules.

The third term in the right-hand side of Eq. (2) can now be rewritten as

$$\prod_{\rho'=1}^{\rho} [\dot{\nu}_{(\rho')}(\boldsymbol{\theta}')]^{n'(\rho')} \sum_{\{[j]\}_{\boldsymbol{\theta}'}} e^{-U_{\{[j]\}_{\boldsymbol{\theta}'}}/kT} = \prod_{\rho'=1}^{\rho} [\dot{\nu}_{(\rho')}(\boldsymbol{\theta}')]^{n'(\rho')} \sum_{\{[j]\}_{\boldsymbol{\theta}'}} \prod_{\rho'=1}^{\rho} \prod_{i=1}^{n'(\rho')} e^{[\dot{E}_{(\rho')}<j_{(\rho'),i}>]_{\boldsymbol{\theta}'}/kT}$$

$$= \prod_{\rho'=1}^{\rho} \prod_{i=1}^{n'(\rho')} \left[\sum_{j=1}^{\dot{\nu}_{(\rho')}(\boldsymbol{\theta}')} e^{[\dot{E}_{(\rho')}<j>]_{\boldsymbol{\theta}'}/kT} \right]_i$$

$$= \prod_{\rho'=1}^{\rho} \left[\sum_{j=1}^{\dot{\nu}_{(\rho')}(\boldsymbol{\theta}')} e^{[\dot{E}_{(\rho')}<j>]_{\boldsymbol{\theta}'}/kT} \right]^{n'(\rho')}$$

$$= \prod_{\rho'=1}^{\rho} [\bar{\tau}_{(\rho')}(\boldsymbol{\theta}') e^{\bar{E}_{(\rho')}(\boldsymbol{\theta}')/kT}]^{n'(\rho')} \tag{15}$$

with

$$\bar{E}_{(\rho')}(\boldsymbol{\theta}') = \sum_{j=1}^{\dot{\nu}_{(\rho')}(\boldsymbol{\theta}')} [\dot{g}_{(\rho')}<j>]_{\boldsymbol{\theta}'} [\dot{E}_{(\rho')}<j>]_{\boldsymbol{\theta}'} \tag{16}$$

$$\ln \bar{\tau}_{(\rho')}(\boldsymbol{\theta}') = - \sum_{j=1}^{\dot{\nu}_{(\rho')}(\boldsymbol{\theta}')} [\dot{g}_{(\rho')}<j>]_{\boldsymbol{\theta}'} \ln [\dot{g}_{(\rho')}<j>]_{\boldsymbol{\theta}'} \tag{17}$$

and

$$[\dot{g}_{(\rho')}<j>]_{\boldsymbol{\theta}'} = \frac{e^{[\dot{E}_{(\rho')}<j>]_{\boldsymbol{\theta}'}/kT}}{\sum_{j=1}^{\dot{\nu}_{(\rho')}(\boldsymbol{\theta}')} e^{[\dot{E}_{(\rho')}<j>]_{\boldsymbol{\theta}'}/kT}} \tag{18}$$

The physical meanings of some parameters involved in Eqs. (15)–(18) are:

$-[\dot{E}_{(\rho')}<j_{(\rho'),i}>]_{\boldsymbol{\theta}'}$ or $-[\dot{E}_{(\rho')}<j>]_{\boldsymbol{\theta}'}$ ($[\dot{E}_{(\rho')}<j_{(\rho'),i}>]_{\boldsymbol{\theta}'}$, $[\dot{E}_{(\rho')}<j>]_{\boldsymbol{\theta}'} > 0$) = interaction energy with adsorbing site(s) of the ith molecule of

component ρ' in the $j_{(\rho'),i}$th configuration, occurring when the surface molecular densities of the respective components are $\theta'_{(1)}, \theta'_{(2)}, \ldots, \theta'_{(\rho)}$; unless necessary, $j_{(\rho'),i}$ is written simply as j.

$[\dot{g}_{(\rho')}<j>]_{\theta'}$ = probability that a molecule of component ρ' takes the jth adsorption configuration when the surface molecular densities of the respective components are $\theta'_{(1)}, \theta'_{(2)}, \ldots, \theta'_{(\rho)}$, showing a Boltzmann distribution.

$\bar{E}_{(\rho')}(\boldsymbol{\theta}')$ = expectation value of $[\dot{E}_{(\rho')}<j>]_{\theta'}$.

$\ln \bar{\tau}_{(\rho')}(\boldsymbol{\theta}')$ = expectation value of $\ln \{1/[\dot{g}_{(\rho')}<j>]_{\theta'}\}$.

By substituting both Eqs. (5′) and (15) into Eq. (2)

$$Z = \frac{M!}{\prod_{\rho'=1}^{\rho} n'_{(\rho')}!\left(M - \sum_{\rho'=1}^{\rho} n'_{(\rho')}\right)!} \left(\frac{n_0 z}{M}\right)^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \prod_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{y_{(\rho'')}[\mathbf{n}'']\}_I$$

$$\times e^{-U'(\boldsymbol{\theta}')/kT} \prod_{\rho'=1}^{\rho} [\bar{\tau}_{(\rho')}(\boldsymbol{\theta}') e^{\bar{E}_{(\rho')}(\boldsymbol{\theta}')/kT}]^{n'_{(\rho')}}$$

$$= \frac{M!}{\prod_{\rho'=1}^{\rho} n'_{(\rho')}!\left(M - \sum_{\rho'=1}^{\rho} n'_{(\rho')}\right)!} \prod_{\rho'=1}^{\rho} \left(\frac{n_0 z}{M} e^{\frac{1}{n'_{(\rho')}} \sum_{n''_{(\rho')}=1}^{n'_{(\rho')}} \ln y_{(\rho')}[\mathbf{n}'']}\right.$$

$$\times e^{\frac{1}{n'_{(\rho')}} \int_0^{n'_{(\rho')}} \ln \bar{\tau}_{(\rho')}(\boldsymbol{\theta}'') dn''_{(\rho')}} e^{-\frac{1}{kT} \frac{1}{n'_{(\rho')}} \int_0^{n'_{(\rho')}} \bar{E}_{(\rho')}(\boldsymbol{\theta}'') dn''_{(\rho')}}$$

$$\left. \times e^{\frac{1}{kT} \frac{1}{n'_{(\rho')}} \int_0^{n'_{(\rho')}} \bar{E}_{(\rho')}(\boldsymbol{\theta}'') dn''_{(\rho')}} \right)^{n'_{(\rho')}} \tag{19}$$

is obtained where

$$\ln \tilde{\tau}_{(\rho')}(\boldsymbol{\theta}'') = \frac{\partial \sum_{\rho''=1}^{\rho} [n''_{(\rho'')} \ln \bar{\tau}_{(\rho'')}(\boldsymbol{\theta}'')]}{\partial n''_{(\rho')}} \tag{20}$$

$$\tilde{E}'_{(\rho')}(\boldsymbol{\theta}'') = \frac{\partial U'(\boldsymbol{\theta}'')}{\partial n''_{(\rho')}} \tag{21}$$

and

$$\tilde{E}_{(\rho')}(\boldsymbol{\theta}'') = \frac{\partial \sum_{\rho''=1}^{\rho} [n''_{(\rho'')}\bar{E}_{(\rho'')}(\boldsymbol{\theta}'')]}{\partial n''_{(\rho')}} \tag{22}$$

The left-hand sides of Eqs. (20)–(22) are partial specific quantities representing the increments of the total quantities $\Sigma_{\rho''=1}^{\rho} [n''_{(\rho'')} \ln \bar{\tau}_{(\rho'')}(\boldsymbol{\theta}'')]$, $U'(\boldsymbol{\theta}'')$, and $\Sigma_{\rho''=1}^{\rho} [n''_{(\rho'')}\bar{E}_{(\rho'')}(\boldsymbol{\theta}'')]$ of the adsorbed system occurring when a molecule of component ρ' is added. Some remarks are made in Appendix II on the derivation of the right-hand side term from the intermediate term in Eq. (19).

In a grand canonical system, the probabilities of occurrence of the $n'_{(\rho')}$ or $\theta'_{(\rho')}$ values, in general, show very sharp distributions around the expectation values $n_{(\rho')}$ or $\theta_{(\rho')}$, respectively, where $\rho' = 1, 2, \ldots, \rho$. Therefore, in Eq. (19), the following substitutions can be executed:

$$\left.\begin{aligned}
&\frac{1}{n'_{(\rho')}} \sum_{n''_{(\rho')}=1}^{n'_{(\rho')}} \ln y_{(\rho')}[\mathbf{n}''] \approx \ln y_{(\rho')}[\mathbf{n}] \equiv \ln y_{(\rho')}(\boldsymbol{\theta}) \\
&\frac{1}{n'_{(\rho')}} \int_0^{n'_{(\rho')}} \ln \tilde{\tau}_{(\rho')}(\boldsymbol{\theta}'')dn''_{(\rho')} \approx \ln \tilde{\tau}_{(\rho')}[\mathbf{n}] \equiv \ln \tilde{\tau}_{(\rho')}(\boldsymbol{\theta}) \\
&\frac{1}{n'_{(\rho')}} \int_0^{n'_{(\rho')}} \tilde{E}'_{(\rho')}(\boldsymbol{\theta}'')dn''_{(\rho')} \approx \tilde{E}'_{(\rho')}[\mathbf{n}] \equiv \tilde{E}'_{(\rho')}(\boldsymbol{\theta})
\end{aligned}\right\} \tag{23}$$

and

$$\frac{1}{n'_{(\rho')}} \int_0^{n'_{(\rho')}} \tilde{E}_{(\rho')}(\boldsymbol{\theta}'')dn''_{(\rho')} \approx \tilde{E}_{(\rho')}[\mathbf{n}] \equiv \tilde{E}_{(\rho')}(\boldsymbol{\theta})$$

A justification for the substitutions of Eq. (23) is given in Appendix III. Rewriting Eq. (19) by using Eq. (23) in which $y_{(\rho')}(\boldsymbol{\theta})$ is represented in terms of $p_{(\rho')}(\boldsymbol{\theta})$ (This can be done by using Eq. 10 where the term $I - 1$ in the denominator can approximately be replaced by I which is now equal to $\Sigma_{\rho''=1}^{\rho} n_{(\rho'')}$.) and substituting Eq. (19) into Eq. (1), we obtain for the final expression of Ξ:

$$\Xi = \sum_{\sum_{\rho'=1}^{\rho} n'_{(\rho')} \le M} \frac{M!}{\prod_{\rho'=1}^{\rho} n'_{(\rho')}! \left(M - \sum_{\rho'=1}^{\rho} n'_{(\rho')}\right)!} \prod_{\rho'=1}^{\rho} \left[\frac{n_0 z}{M} e^{\mu_{(\rho')}/kT} \right.$$

$$\left. \times \frac{p_{(\rho')}(\boldsymbol{\theta})}{1 - \frac{1}{M}\sum_{\rho''=1}^{\rho} n_{(\rho'')}} \tilde{\tau}_{(\rho')}(\boldsymbol{\theta}) e^{-\tilde{E}'_{(\rho')}(\boldsymbol{\theta})/kT} e^{\tilde{E}_{(\rho')}(\boldsymbol{\theta})/kT} \right]^{n'_{(\rho')}}$$

$$= \left\{ 1 + \sum_{\rho'=1}^{\rho} \left[\frac{n_0 z}{M} e^{\mu_{(\rho')}/kT} \frac{p_{(\rho')}(\boldsymbol{\theta})}{1 - \frac{1}{M}\sum_{\rho''=1}^{\rho} n_{(\rho'')}} \tilde{\tau}_{(\rho')}(\boldsymbol{\theta}) \right.\right.$$

$$\left.\left. \times e^{-\tilde{E}'_{(\rho')}(\boldsymbol{\theta})/kT} e^{\tilde{E}_{(\rho')}(\boldsymbol{\theta})/kT} \right] \right\}^{M} \tag{24}$$

Since the probability that $n'_{(\rho')}$ molecules of component ρ' are adsorbed on the adsorbent surface is equal to $e^{n'_{(\rho')}\mu_{(\rho')}/kT} Z/\Xi$, $n_{(\rho')}$ can be represented by using Eq. (24) as

$$n_{(\rho')} = \frac{1}{\Xi} \sum_{\sum_{\rho'=1}^{\rho} n'_{(\rho')} \le M} n'_{(\rho')} e^{n'_{(\rho')}\mu_{(\rho')}/kT} Z$$

$$= kT \frac{\partial}{\partial \mu_{(\rho')}} \ln \Xi$$

$$= \frac{n_0 z e^{\mu_{(\rho')}/kT} \frac{p_{(\rho')}(\boldsymbol{\theta})}{1 - \frac{1}{M}\sum_{\rho''=1}^{\rho} n_{(\rho'')}} \tilde{\tau}_{(\rho')}(\boldsymbol{\theta}) e^{-\tilde{E}'_{(\rho')}(\boldsymbol{\theta})/kT} e^{\tilde{E}_{(\rho')}(\boldsymbol{\theta})/kT}}{1 + \sum_{\rho'=1}^{\rho} \left[\frac{n_0 z}{M} e^{\mu_{(\rho')}/kT} \frac{p_{(\rho')}(\boldsymbol{\theta})}{1 - \frac{1}{M}\sum_{\rho''=1}^{\rho} n_{(\rho'')}} \tilde{\tau}_{(\rho')}(\boldsymbol{\theta}) e^{-\tilde{E}'_{(\rho')}(\boldsymbol{\theta})/kT} e^{\tilde{E}_{(\rho')}(\boldsymbol{\theta})/kT} \right]}$$

$$(\rho' = 1, 2, \ldots, \rho) \tag{25}$$

Equation (25) can be rewritten after some calculations (Appendix IV) as

$$x'_{(\rho')}\lambda_{(\rho')} = \frac{\theta_{(\rho')}}{zp_{(\rho')}(\boldsymbol{\theta})\bar{\tau}_{(\rho')}(\boldsymbol{\theta})} e^{\tilde{E}'_{(\rho')}(\boldsymbol{\theta})/kT} e^{-\tilde{E}_{(\rho')}(\boldsymbol{\theta})/kT} \qquad (\rho' = 1, 2, \cdots, \rho) \tag{25'}$$

in which

$$\lambda_{(\rho')} = e^{\mu(\rho')/kT} \tag{26}$$

represents the absolute activity for component ρ' being approximately proportional to the concentration in solution. Equation (25'), which can be considered to be simultaneous equations for $\theta_{(1)}, \theta_{(2)}, \ldots, \theta_{(\rho)}$, represents the adsorption isotherms for the components $1, 2, \ldots, \rho$ of the mixture.

(B) Convenient Expression of the Adsorption Isotherms, Eq. (25')

In Eq. (25'), in contrast with $p_{(\rho')}(\boldsymbol{\theta})$ fulfilling Eq. (9), $\bar{\tau}_{(\rho')}(\boldsymbol{\theta})$, $\tilde{E}'_{(\rho')}(\boldsymbol{\theta})$, and $\tilde{E}_{(\rho')}(\boldsymbol{\theta})$ can be assumed to fulfill the relationships

$$\lim_{\sum_{\rho''=1}^{\rho} \theta_{(\rho'')} \to 0} \bar{\tau}_{(\rho')}(\boldsymbol{\theta}) = \lim_{\sum_{\rho''=1}^{\rho} \theta_{(\rho'')} \to 0} \bar{\tau}_{(\rho')}(\boldsymbol{\theta}) = \tau_{(\rho')} \tag{27}$$

$$\lim_{\sum_{\rho''=1}^{\rho} \theta_{(\rho'')} \to 0} \tilde{E}'_{(\rho')}(\boldsymbol{\theta}) = 0 \tag{28}$$

and

$$\lim_{\sum_{\rho''=1}^{\rho} \theta_{(\rho'')} \to 0} \tilde{E}_{(\rho')}(\boldsymbol{\theta}) = \lim_{\sum_{\rho''=1}^{\rho} \theta_{(\rho'')} \to 0} \bar{E}_{(\rho')}(\boldsymbol{\theta}) = E_{(\rho')} \tag{29}$$

where $\ln \tau_{(\rho')}$ and $E_{(\rho')}$ are positive constants representing the entropy factor per molecule of component ρ' and the absolute value of the interaction energy with adsorbing site(s) per molecule of component ρ' occurring provided the molecule is isolated from the other molecules on the adsorbent surface, respectively.

Let us introduce the parameters

$$p^*_{(\rho')}(\boldsymbol{\theta}) = \frac{\bar{\tau}_{(\rho')}(\boldsymbol{\theta})}{\tau_{(\rho')}} p_{(\rho')}(\boldsymbol{\theta}) \tag{30}$$

and

$$E^*_{(\rho')}(\boldsymbol{\theta}) = \tilde{E}'_{(\rho')}(\boldsymbol{\theta}) - \tilde{E}_{(\rho')}(\boldsymbol{\theta}) + E_{(\rho')} \tag{31}$$

Similarly to the case of a single component system (*1*), $\tau_{(\rho')}$ would decrease, in many instances, with an increase of $\Sigma^{\rho}_{\rho''=1}\theta_{(\rho'')}$ (in relationship with a decrease of $\dot{\nu}_{(\rho')}$; see the explanation of Eq. 14). Therefore, the relationships

$$\left.\begin{aligned} &\lim_{\sum_{\rho''=1}^{\rho}\theta_{(\rho'')}\to 0} p^*_{(\rho')}(\boldsymbol{\theta}) = 1 \\ &\text{and} \\ &\lim_{\sum_{\rho''=1}^{\rho}\theta_{(\rho'')}\to\left[\sum_{\rho''=1}^{\rho}\theta_{(\rho'')}\right]_{\max}} p^*_{(\rho')}(\boldsymbol{\theta}) = 0 \end{aligned}\right\} \tag{32}$$

would hold, and $p^*(\boldsymbol{\theta})$ would decrease with an increase of $\Sigma^{\rho}_{\rho''=1}\theta_{(\rho'')}$. Especially if the adsorption configuration of a molecule is independent of $\boldsymbol{\theta}$, $\tilde{\tau}_{(\rho')}$ is always equal to $\tau_{(\rho')}$, and $p_{(\rho')}$ or $p^*_{(\rho')}$ (Eq. 30) represents a probability (see the explanation of Eq. 8). Corresponding to Eq. (29), we have

$$\lim_{\sum_{\rho''=1}^{\rho}\theta_{(\rho'')}\to 0} E^*_{(\rho')}(\theta) = 0 \tag{33}$$

Similarly to the case of a single component system (*1*), $E^*_{(\rho')}(\boldsymbol{\theta})$ can be called a mutual interaction energy per molecule of component ρ'. It can be considered that $p^*_{(\rho')}(\boldsymbol{\theta})$ represents the geometrical interaction factor for a molecule of component ρ' with any other molecules on the adsorbent surface.

Equation (25′) can now be rewritten as

$$x'_{(\rho')}\lambda_{(\rho')} = \Psi_{(\rho')}(\boldsymbol{\theta})e^{-E_{(\rho')}/kT} \qquad (\rho' = 1, 2, \cdots, \rho) \tag{34}$$

in which

$$\Psi_{(\rho')}(\boldsymbol{\theta}) = \frac{\theta_{(\rho')}e^{E^{\dagger}_{(\rho')}(\boldsymbol{\theta})/kT}}{z\tau_{(\rho')}p^*_{(\rho')}(\boldsymbol{\theta})} \tag{35}$$

If $\Sigma_{\rho''=1}^{\rho} \theta_{(\rho'')}$ is small, Eq. (35) reduces to

$$\Psi_{(\rho')}(\boldsymbol{\theta}) \approx \Psi_{(\rho')}(0, \cdots, 0, \theta_{(\rho')}, 0, \cdots, 0) \approx \frac{\theta_{(\rho')}}{z\tau_{(\rho')}} \tag{36}$$

and the adsorption and desorption of the molecules of each component of the mixture occur independently.

Finally, if the molecule has a rigid structure and if functional adsorption groups are arranged on the molecular surface, $E_{(\rho')}$ can be represented as

$$E_{(\rho')} = x_{(\rho')}\varepsilon \tag{37}$$

in which $-\varepsilon$ ($\varepsilon > 0$) is the adsorption energy of a functional group onto one of the sites of the adsorbent. $x_{(\rho')}$ is the average number of functional groups per molecule of component ρ' that react with sites of the adsorbent provided the molecule is isolated. $x_{(\rho')}$ and $\ln \tau_{(\rho')}$ can be written as

$$x_{(\rho')} = \sum_{j=1}^{\nu(\rho')} g_{(\rho')}\langle j \rangle \cdot x_{(\rho')}\langle j \rangle \tag{38}$$

and

$$\ln \tau_{(\rho')} = -\sum_{j=1}^{\nu(\rho')} g_{(\rho')}\langle j \rangle \cdot \ln g_{(\rho')}\langle j \rangle \tag{39}$$

where

$$g_{(\rho')}\langle j \rangle = \frac{e^{x_{(\rho')}\langle j \rangle \varepsilon/kT}}{\sum_{j=1}^{\nu(\rho')} e^{x_{(\rho')}\langle j \rangle \varepsilon/kT}} \tag{40}$$

$x_{(\rho')}\langle j \rangle$ represents the number of functional groups per molecule of component ρ' that react with sites of the adsorbent when the molecule is taking the jth configuration [cf. footnote in Theoretical Section (C) of Ref. *1*].

(C) Another Method for the Derivation of Eq. (25′)

Assuming *a priori* that the total numbers $n_{(1)}, n_{(2)}, \ldots, n_{(\rho)}$ of the molecules of the respective components of the mixture on the adsorbent surface are constant and that the adsorbed molecules constitute a canonical system, the Helmholtz free energy, F, of the system can be calculated. The chemical potentials $\mu_{(1)}, \mu_{(2)}, \ldots, \mu_{(\rho)}$ for the respective molecular components of the adsorbed system can be derived from the relationships $\mu_{(1)} = \partial F/\partial n_{(1)}, \mu_{(2)} = \partial F/\partial n_{(2)}, \ldots, \mu_{(\rho)} = \partial F/\partial n_{(\rho)}$ wehreas the chemical potentials $\mu^\circ_{(1)}, \mu^\circ_{(2)}, \ldots, \mu^\circ_{(\rho)}$ in solution that are in equilibrium with the adsorbed system can be represented as $\mu^\circ_{(1)} = kT \ln \lambda_{(1)}, \mu^\circ_{(2)} = kT \ln \lambda_{(2)}, \ldots, \mu^\circ_{(\rho)} = kT \ln \lambda_{(\rho)}$ in which $\lambda_{(1)}, \lambda_{(2)}, \ldots, \lambda_{(\rho)}$ are approximately proportional to the molecular concentrations of the respective components in solution. Equation (25′) can be derived from the equilibrium conditions: $\mu_{(1)} = \mu^\circ_{(1)}, \mu_{(2)} = \mu^\circ_{(2)}, \ldots, \mu_{(\rho)} = \mu^\circ_{(\rho)}$.

DISCUSSION

See the Discussion Section in Part III of this series (*2*).

APPENDIX I

Since ω is a state quantity, $\prod_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\phi_{(\rho'')}[\mathbf{n''}]\}_I$ (Eq. 5), $\prod_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{p_{(\rho'')}[\mathbf{n''}]\}_I$ and $\prod_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{y_{(\rho'')}[\mathbf{n''}]\}_I$ (Eq. 5′) are also state quantities. Thus, for a serial variation in the I value: $1, 2, \ldots, \Sigma^{\rho}_{\rho'=1} n'_{(\rho')}$, there are a number of ways of variation of the corresponding set $(n''_{(1)}, n''_{(2)}, \ldots, n''_{(\rho)})$. The $\prod_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\quad\}_I$ values are uniquely determined by the final set $(n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho)})$ whatever may be the way through which the final set is attained.

APPENDIX II

The derivation of the right-hand side term from the intermediate term in Eq. (19) has been carried out by using the following relationships:

$$\sum_{\rho'=1}^{\rho} \sum_{I=1}^{n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_I = \sum_{\rho'=1}^{\rho} \sum_{n''_{(\rho')}=1}^{n'_{(\rho')}} \ln y_{(\rho')}[\mathbf{n}''] \tag{a1}$$

$$\sum_{\rho'=1}^{\rho} [n'_{(\rho')} \ln \bar{\tau}_{(\rho')}(\boldsymbol{\theta}')] = \sum_{\rho'=1}^{\rho} \int_0^{n'_{(\rho')}} \ln \tilde{\tau}_{(\rho')}(\boldsymbol{\theta}'') dn''_{(\rho')} \tag{a2}$$

$$U'(\boldsymbol{\theta}') = \sum_{\rho'=1}^{\rho} \int_0^{n'_{(\rho')}} \tilde{E}'_{(\rho')}(\boldsymbol{\theta}'') dn''_{(\rho')} \tag{a3}$$

and

$$\sum_{\rho'=1}^{\rho} [n'_{(\rho')} \bar{E}_{(\rho')}(\boldsymbol{\theta}')] = \sum_{\rho'=1}^{\rho} \int_0^{n'_{(\rho')}} \tilde{E}_{(\rho')}(\boldsymbol{\theta}'') dn''_{(\rho')} \tag{a4}$$

Proof of Eqs. (a2)–(a4): In general, for an arbitrary function $f(n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho)})$, the relationship

$$f(n'_{(1)}, n'_{(2)}, \cdots, n'_{(\rho)}) = \sum_{\rho'=1}^{\rho} \int_0^{n'_{(\rho')}} \frac{\partial f(n''_{(1)}, n''_{(2)}, \cdots, n''_{(\rho)})}{\partial n''_{(\rho')}} dn''_{(\rho')} \tag{a5}$$

is fulfilled. Therefore, considering in Eqs. (20)–(22)

$$f(n''_{(1)}, n''_{(2)}, \cdots, n''_{(\rho)}) = \sum_{\rho''=1}^{\rho} [n''_{(\rho'')} \ln \bar{\tau}_{(\rho'')}(\boldsymbol{\theta}'')] \tag{a6}$$

$$f(n''_{(1)}, n''_{(2)}, \cdots, n''_{(\rho)}) = U'(\boldsymbol{\theta}'') \tag{a7}$$

and

$$f(n''_{(1)}, n''_{(2)}, \cdots, n''_{(\rho)}) = \sum_{\rho''=1}^{\rho} [n''_{(\rho'')} \bar{E}_{(\rho'')}(\boldsymbol{\theta}'')] \tag{a8}$$

then, Eqs. (a2)–(a4) can immediately be obtained, respectively.

Proof of Eq. (a1): As will be proven below, we have a relationship

$$\ln y_{(\rho')}[\mathbf{n}'] = \frac{\partial \sum_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_I}{\partial n'_{(\rho')}} \tag{a9}$$

Therefore, by considering

$$f(n'_{(1)}, n'_{(2)}, \cdots, n'_{(\rho)}) = \sum_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_I \tag{a10}$$

and by replacing the integral with a sum, Eq. (a1) can immediately be obtained.

The proof of Eq. (a9) is given below. Thus, let us consider two states 1 and 2 on the adsorbent surface. In State 1 there are $n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho'-1)}, n'_{(\rho')} - \Delta n'_{(\rho')}, n'_{(\rho'+1)}, \ldots, n'_{(\rho)}$ molecules of the respective components of the mixture on the adsorbent surface, where $0 < \Delta n'_{(\rho')} \ll \Sigma_{\rho''=1}^{\rho} n'_{(\rho'')}$, and, in State 2, there are $n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho'-1)}, n'_{(\rho')}, n'_{(\rho'+1)}, \ldots, n'_{(\rho)}$ corresponding molecules. We consider to realize State 2 by adding successively $\Sigma_{\rho'=1}^{\rho} n'_{(\rho')}$ molecules of the mixture either through State 1 (Way I') or arbitrarily (Way I); Way I may or may not pass through State 1. Since $\sum_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_I$ is a state quantity (see Appendix I), it is always equal to $\sum_{I'=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_{I'}$ from which it follows that

$$\sum_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_I$$

$$= \sum_{I'=1}^{\left(\sum_{\rho'=1}^{\rho} n'_{(\rho')}\right)-\Delta n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_{I'} + \sum_{I'=\left(\sum_{\rho'=1}^{\rho} n'_{(\rho')}\right)-\Delta n'_{(\rho')}+1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_{I'}$$

$$\approx \sum_{I'=1}^{\left(\sum_{\rho'=1}^{\rho} n'_{(\rho')}\right)-\Delta n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_{I'} + \Delta n'_{(\rho')} \ln y_{(\rho')}[\mathbf{n}'] \tag{a11}$$

Equation (a11) can be rewritten as

$$\frac{\partial \sum_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_I}{\partial n'_{(\rho')}}$$

$$\equiv \frac{\sum_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_I - \sum_{I'=1}^{\left(\sum_{\rho'=1}^{\rho} n'_{(\rho')}\right)-\Delta n'_{(\rho')}} \{\ln y_{(\rho'')}[\mathbf{n}'']\}_{I'}}{\Delta n'_{(\rho')}}$$

$$= \ln y_{(\rho')}[\mathbf{n}'] \tag{a11'}$$

which is Eq. (a9) itself.

APPENDIX III

Introducing the parameter:

$$\ln X_{(\rho')}[\mathbf{n}''] \equiv \ln \frac{n_0 z}{M} + \frac{\mu_{(\rho')}}{kT} + \ln y_{(\rho')}[\mathbf{n}''] + \ln \tilde{\tau}_{(\rho')}[\mathbf{n}''] - \frac{\tilde{E}'_{(\rho')}[\mathbf{n}'']}{kT} + \frac{\tilde{E}_{(\rho')}[\mathbf{n}'']}{kT} \tag{a12}$$

Eq. (1) into which Eq. (19) is substituted can be written as

$$\Xi = \sum_{\substack{\rho \\ \sum_{\rho'=1} n'_{(\rho')} < M}} \psi_1(n'_{(1)}, n'_{(2)}, \cdots, n'_{(\rho)}) \tag{a13}$$

where

$$\psi_1(n'_{(1)}, n'_{(2)}, \cdots, n'_{(\rho)}) = \frac{M!}{\prod_{\rho'=1}^{\rho} n'_{(\rho')}! \left(M - \sum_{\rho'=1}^{\rho} n'_{(\rho')}\right)!} \prod_{\rho'=1}^{\rho} \prod_{n''_{(\rho')}=1}^{n'_{(\rho')}} X_{(\rho')}[\mathbf{n}''] \tag{a14}$$

On the other hand, Eq. (24) (i.e., Eq. 1 into which Eq. 19 rewritten by using Eq. 23 is substituted) can be rewritten as

$$\Xi = \sum_{\substack{\rho \\ \sum_{\rho'=1} n'_{(\rho')} < M}} \psi_2(n'_{(1)}, n'_{(2)}, \cdots, n'_{(\rho)}) \tag{a15}$$

where

$$\psi_2(n'_{(1)}, n'_{(2)}, \cdots, n'_{(\rho)}) = \frac{M!}{\prod_{\rho'=1}^{\rho} n'_{(\rho')}! \left(M - \sum_{\rho'=1}^{\rho} n'_{(\rho')}\right)!} \prod_{\rho'=1}^{\rho} \{X_{(\rho')}[\mathbf{n}]\}^{n'_{(\rho')}} \tag{a16}$$

Statistical mechanics, in general, concludes that, when $M \gg 1$, $\psi_1(n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho)})$ shows a very sharp distribution around a set $(n_{(1)}, n_{(2)}, \ldots, n_{(\rho)})$, the elements of which represent the expectation values of $n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho)}$, respectively, and that the set $(n_{(1)}, n_{(2)}, \ldots, n_{(\rho)})$ gives ψ_1 a maximum value. $n_{(1)}, n_{(2)}, \ldots, n_{(\rho)}$ can be represented as solutions of the simultaneous equations

$$\frac{\partial \ln \psi_1}{\partial n'_{(\rho')}} = 0 \qquad (\rho' = 1, 2, \cdots, \rho) \tag{a17}$$

Thus, calculating the left-hand side of Eq. (a17) by using Stirling's approximation and the relationships

$$\sum_{\rho'=1}^{\rho} \sum_{n''_{(\rho')}=1}^{n'_{(\rho')}} \ln X_{(\rho')}[\mathbf{n}''] = \sum_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\ln X_{(\rho'')}[\mathbf{n}'']\}_I \tag{a18}$$

and

$$\frac{\partial \sum_{I=1}^{\sum_{\rho'=1}^{\rho} n'_{(\rho')}} \{\ln X_{(\rho'')}[\mathbf{n}'']\}_I}{\partial n'_{(\rho')}} = \ln X_{(\rho')}[\mathbf{n}'] \tag{a19}$$

which correspond to Eqs. (a1) and (a9) in Appendix II, respectively, and writing $n_{(1)}, n_{(2)}, \ldots, n_{(\rho)}$ instead of $n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho)}$, respectively, then

$$-\ln n_{(\rho')} + \ln\left(M - \sum_{\rho''=1}^{\rho} n_{(\rho'')}\right) + \ln X_{(\rho')}[\mathbf{n}] = 0 \qquad (\rho' = 1, 2, \cdots, \rho) \tag{a20}$$

is obtained; $n_{(1)}, n_{(2)}, \ldots, n_{(\rho)}$ can be considered to be solutions of the simultaneous equations, Eq. (a20).

When $M \gg 1$, $\psi_2(n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho)})$ also shows a very sharp distribution around a set $(n^*_{(1)}, n^*_{(2)}, \ldots, n^*_{(\rho)})$, the elements of which represent the expectation values of $n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho)}$, respectively, and the set $(n^*_{(1)}, n^*_{(2)}, \ldots, n^*_{(\rho)})$ gives ψ_2 a maximum value. $n^*_{(1)}, n^*_{(2)}, \ldots, n^*_{(\rho)}$ can be represented as solutions of the simultaneous equations

$$\frac{\partial \ln \psi_2}{\partial n'_{(\rho')}} = 0 \qquad (\rho' = 1, 2, \cdots, \rho) \tag{a21}$$

Thus, calculating the left-hand side of Eq. (a21) by using Stirling's approximation, and writing $n^*_{(1)}, n^*_{(2)}, \ldots, n^*_{(\rho)}$ instead of $n'_{(1)}, n'_{(2)}, \ldots, n'_{(\rho)}$, respectively, then

$$-\ln n^*_{(\rho')} + \ln\left(M - \sum_{\rho''=1}^{\rho} n^*_{(\rho'')}\right) + \ln X_{(\rho')}[\mathbf{n}] = 0 \qquad (\rho' = 1, 2, \cdots, \rho) \tag{a22}$$

is obtained; $n^*_{(1)}, n^*_{(2)}, \ldots, n^*_{(\rho)}$ can be considered to be solutions of the simultaneous equations, Eq. (a22).

It is evident that the solutions $n_{(1)}, n_{(2)}, \ldots, n_{(\rho)}$ of Eq. (a20) are equal to the solutions $n^*_{(1)}, n^*_{(2)}, \ldots, n^*_{(\rho)}$ of Eq. (a22), justifying the substitutions of Eq. (23).

APPENDIX IV

Derivation of Eq. (25') from Eq. (25): Dividing an equation for component ρ' by another for component ρ'' in Eq. (25) leads to

$$x'_{(\rho')}\lambda_{(\rho')}\left[\frac{\theta_{(\rho')}}{zp_{(\rho')}(\boldsymbol{\theta})\tilde{\tau}_{(\rho')}(\boldsymbol{\theta})}\, e^{\tilde{E}'_{(\rho')}(\boldsymbol{\theta})/kT} e^{-\tilde{E}_{(\rho')}(\boldsymbol{\theta})/kT}\right]^{-1} = \text{constant} \qquad \text{(a23)}$$

By substituting Eq. (a23) into Eq. (25), the value of the constant is determined to be unity, and Eq. (25') is derived.

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