

A New Approach to Interfacial Energy. 2. Interfacial Energies of Different Interfaces under the Influence of Adsorption

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On the basis of the fundamental equation of the specific interfacial energy γ formulated in the preceding part 1 (*J. Colloid Interface Sci.* **1996**, *181*, 259; **1996**, *183*, 299), individual concrete equations of γ for different interfaces in liquid–liquid, solid–liquid, solid–gas, and liquid–gas systems under the influence of adsorption have been derived, according to the inherent natures of these interfaces. For liquid–liquid and liquid–gas systems, the essential difference in behavior of ordinary adsorptives and amphiphilic compounds is discussed in detail. For solid–liquid and solid–gas systems, homogeneous and heterogeneous solid surfaces are newly defined and treated distinctively. For solid–gas and liquid–gas systems, in particular, a new concept of vacancies as imaginary matrix molecules of the gas phases is introduced to deal with these specific interfaces in the same way as the other kinds of interfaces on the basis of the fundamental equation. Lastly, the limitations of the original Langmuir and Szyszkowski equations and some basic problems of conventional thermodynamics in itself are discussed. As a result, it has been disclosed that all kinds of interfacial energies can be described in consistency as a function of the individual behavior of the interfacial molecules on the basis of the new fundamental equation and that the difference in molecular size and shape of each component in a given system is a dominant factor in the characteristic behavior of the interfacial energies of different interfaces.

1. Introduction

In part 1,¹ the general formula of the interfacial energy has been derived on the basis of a new approach to the nature of the interfacial energy. Since the theory is significantly different from the conventional treatment, it seems necessary to summarize the background and main conclusions of part 1 prior to advancing to part 2.

In a inhomogeneous system, the internal energy of the interface phase, U^σ , at absolute temperature T and pressure P is usually written as

$$U^\sigma = TS^\sigma - PV^\sigma + \gamma A^\sigma + \sum \mu_i^{\sigma'} n_i^\sigma \quad (1.1)$$

where S^σ , V^σ , γ , A^σ , $\mu_i^{\sigma'}$ and n_i^σ are the entropy, volume, specific interfacial energy or surface tension, surface area, chemical potential of component i , and mole number of component i in the interface phase.^{2,3} From the total differential of eq 1.1, one obtains

$$dG^{\sigma'} = -S^\sigma dT + V^\sigma dP - A^\sigma d\gamma + \sum \mu_i^{\sigma'} dn_i^\sigma \quad (1.2)$$

where $G^{\sigma'} \equiv \sum \mu_i^{\sigma'} n_i^\sigma$. Hence, it follows that

$$\mu_i^{\sigma'} = \left(\frac{\partial G^{\sigma'}}{\partial n_i^\sigma} \right)_{T,P,\gamma,n_j^\sigma} \quad (1.3)$$

where n_j^σ represents the mole number of arbitrary interfacial component other than component i . In this partial differential of $G^{\sigma'}$, the variables T , P , γ , and n_j^σ for all interfacial components but n_i^σ are fixed. On the other hand, corresponding quantities in a homogeneous bulk phase α are given by

$$U^\alpha = TS^\alpha - PV^\alpha + \sum \mu_i^\alpha n_i^\alpha \quad (1.4)$$

and

$$\mu_i^\alpha = \left(\frac{\partial G^\alpha}{\partial n_i^\alpha} \right)_{T,P,n_j^\alpha} \quad (1.5)$$

where $G^\alpha (\equiv \sum \mu_i^\alpha n_i^\alpha)$ is the Gibbs free energy of phase α .

As is obvious from eq 1.5, the state of phase α and thus the state quantity such as μ_i^α are determined by only T , P , and n_i^α for all components in phase α as long as the interactive potential field from the neighboring phases is fixed. Similarly, if we consider a sufficiently thin layer, parallel to the interface of the two bulk phases, to be regarded as homogeneous in the interfacial zone, the state of the homogeneous layer and thus its state quantities such as chemical potential of each component, are determined by only T , P , and n_i for all components in the layer, irrespective of γ . Hence, if we define a certain domain as an interface phase and if the state of each constituent layer is determined in this way, the state of the interface phase must also be determined regardless of γ . Despite this fact, even the internal energy of the interface phase, U^σ , as well as G^σ and $\mu_i^{\sigma'}$ in eqs 1.1–1.3 cannot be determined only by the state of the interface unless the states of the neighboring bulk phases are specified, since the state functions of the interface involve an additional variable γ which is the excess energy of the interfacial molecules per unit area relative to the free energies of the corresponding molecules in the bulk phases. Moreover, it is physically impossible to change only n_i^σ without changing γ in the partial differential in eq 1.3, since the excess energy of interface, γ , is borne by the individual interfacial molecules. In short, it is incorrect to treat γ as an independent variable for

determining the state of an interface, and thus $\mu_i^{\sigma'}$ defined in eq 1.3 has no significance as an intrinsic chemical potential of component i.

Since there is no reason to write the internal energy and chemical potentials of components in a homogeneous thin layer at a position z in the interfacial zone in different ways from those in a bulk phase, we may write them as

$$U^z = TS^z - P^z V^z + \sum \mu_i^z n_i^z \quad (1.6)$$

and

$$\mu_i^z = \left(\frac{\partial G^z}{\partial n_i^z} \right)_{T,P,n_j^z} \quad (1.7)$$

where $G^z (\equiv \sum \mu_i^z n_i^z)$ is the Gibbs free energy of the layer at z and μ_i^z is the intrinsic chemical potential of component i in the layer. If we define the overall chemical potential of component i in the interface phase ranging from $z = -\delta$ to $z = +\delta$ for the z axis taken perpendicular to the interface, we may write the overall chemical potential of component i in the interface phase as

$$\mu_i^\sigma = \frac{\int_{-\delta}^{+\delta} A_z m_i^z \mu_i^z dz}{n_i^\sigma} \quad (1.8)$$

where A_z is the cross-sectional area at z , m_i^z is the volume density of component i at z , and n_i^σ is the total mole number of component i in the interface phase. Hence, the internal energy of the interface is given in the same way as that of a bulk phase as

$$U^\sigma = TS^\sigma - P^\sigma V^\sigma + \sum \mu_i^\sigma n_i^\sigma \quad (1.9)$$

If we write eq 1.8 on the basis of the *interfacial double layer model* proposed in part 1, in which the interface is assumed to be composed of the two adjoining surface layers of the different bulk phases from insights into the nature of the actual interface,

$$\mu_i^\sigma \equiv \frac{\mu_i^{\sigma_A} n_i^{\sigma_A} + \mu_i^{\sigma_B} n_i^{\sigma_B}}{n_i^{\sigma_A} + n_i^{\sigma_B}} \quad (1.10)$$

where the superscripts σ_A and σ_B indicate the adjoining surface layers of bulk phases α and β , respectively; $n_i^{\sigma_A} + n_i^{\sigma_B} = n_i^\sigma$.

On the other hand, it has theoretically been proven in part 1 that all chemical potentials of the components in the interface cannot be equal to the respective chemical potentials in the bulk phases even at equilibrium between the interface and the bulks, in contrast to the equilibrium between bulk phases in which the chemical potentials of each component in the different bulk phases are equal (see the Introduction of ref 1). In addition, there is no doubt that the total free energy of the interfacial molecules is higher than that of the same numbers of the respective bulk molecules, as obvious from plenty of evidence such as the interfacial tension, the Gibbs–Thomson effect, etc., despite the fact that the internal energy U^σ and the Gibbs free energy G^σ can be defined in exactly the same way as those in the bulk phase. Hence, the origin of the interfacial energy must be attributed to the free energy difference between the interface and the bulk phases due to the difference in chemical potential of each component between the interface and the bulk phases,

and thus, we have concluded that the total of the chemical potential differences between the interface and the bulk phases for all interfacial components per unit area is equal to γ . Namely,

$$\gamma A^\sigma = \sum (\mu_i^\sigma - \mu_i) n_i^\sigma \quad (1.11)$$

where μ_i is the chemical potential of component i in the bulk phases α and β , averaged for $n_i^{\sigma_A}$ and $n_i^{\sigma_B}$ as

$$\mu_i = \frac{\mu_i^\alpha n_i^{\sigma_A} + \mu_i^\beta n_i^{\sigma_B}}{n_i^{\sigma_A} + n_i^{\sigma_B}} \quad (1.12)$$

Thus eq 1.11 can be applied to nonequilibrium systems as well. If we rewrite eq 1.9 using eq 1.11, we obtain

$$\begin{aligned} U^\sigma &= TS^\sigma - P^\sigma V^\sigma + \sum (\mu_i^\sigma - \mu_i) n_i^\sigma + \sum \mu_i n_i^\sigma \\ &= TS^\sigma - P^\sigma V^\sigma + \gamma A^\sigma + \sum \mu_i n_i^\sigma \end{aligned} \quad (1.13)$$

Thus, as long as we use the intrinsic chemical potentials of components regardless of their positions, $\mu_i^{\sigma'}$ in eq 1.1 must always be the chemical potential of component i in the bulk phases, μ_i^α , even when the system is not in equilibrium, in contrast to the conventional treatment in which it is presumed that $\mu_i^{\sigma'} = \mu_i^\sigma = \mu_i^\beta$ in eqs 1.1 and 1.2 on the assumption of the system being in equilibrium. The conventional mistreatment comes from the inadequate definition of the interfacial chemical potential in eq 1.3 as a result of the interpretation of γ as an independent variable. Here it must be noted that $\mu_i = \mu_i^\alpha = \mu_i^\beta$ at equilibrium, but generally $\mu_i^\sigma \neq \mu_i$ even at equilibrium. This can be derived as follows.

The change of the Gibbs free energy of the system with the mass transfer between interface σ and the bulk phases α and β is given by

$$\begin{aligned} dG &= \sum (\mu_i^\sigma dn_i^\sigma + \mu_i dn_i) = \sum (\mu_i^\sigma - \mu_i) dn_i^\sigma \\ &= \sum' A^\sigma [N_i^\sigma (\mu_i^{\sigma_A} - \mu_i^\alpha) - N_A^\sigma (\mu_A^{\sigma_A} - \mu_A^\alpha)] dy_i^{\sigma_A} + \\ &\quad \sum' A^\sigma [N_j^\sigma (\mu_j^{\sigma_B} - \mu_j^\beta) - N_B^\sigma (\mu_B^{\sigma_B} - \mu_B^\beta)] dy_j^{\sigma_B} \end{aligned} \quad (1.14)$$

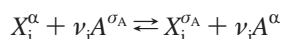
where Σ' means summation for only nonmatrix components, as different from Σ for all components; A and B are the matrix components of phases α and β , respectively; dn_i is the total change of the mole number of component i in phases α and β ($dn_i = -dn_i^\sigma$); N_i^σ and N_j^σ are the maximum surface densities of components i and j in surface layers σ_A and σ_B , respectively; $y_i^{\sigma_A}$ and $y_j^{\sigma_B}$ are the area fractions of components i and j in surface layers σ_A and σ_B , respectively. Typically, the matrix and nonmatrix components in a liquid phase are the solvent and solute species, respectively. Here it should be noted that, while $y_i^{\sigma_A}$ and $y_j^{\sigma_B}$ for nonmatrix components can independently be changed, $y_A^{\sigma_A}$ and $y_B^{\sigma_B}$ for the matrix components are dependent variables, since $dy_A^{\sigma_A} = -\Sigma' dy_i^{\sigma_A}$ and $dy_B^{\sigma_B} = -\Sigma' dy_j^{\sigma_B}$ from $\Sigma y_i^{\sigma_A} = \Sigma y_j^{\sigma_B} = 1$. Since G must take the minimum value at equilibrium, $dG = 0$ for the independent change of $y_i^{\sigma_A}$ and $y_j^{\sigma_B}$ of nonmatrix components, and thus it must hold for arbitrary nonmatrix components i and j that

$$N_i^\sigma (\mu_i^{\sigma_A} - \mu_i^\alpha) = N_A^\sigma (\mu_A^{\sigma_A} - \mu_A^\alpha) (= \gamma_A) \quad (1.15a)$$

and

$$N_j^\sigma(\mu_j^{\sigma_B} - \mu_j^\beta) = N_B^\sigma(\mu_B^{\sigma_B} - \mu_B^\beta) (= \gamma_B) \quad (1.15b)$$

where γ_A and γ_B in parentheses are the specific surface energies of surface layers σ_A and σ_B , respectively, as constituents of the specific interfacial energy γ ($=\gamma_A + \gamma_B$), as is obvious if one refers to eq 1.11. Equations 1.15a and 1.15b are the equilibrium conditions between the σ_A layer and α phase and between the σ_B layer and β phase, respectively. Equations 1.15a and 1.15b can be derived from the adsorption equilibrium as well. For example, as one may regard adsorption as a substitutional reaction in which ν_i molecules of matrix component A in surface later σ_A are released by adsorption of one molecule of adsorbate X_i from bulk phase α , the chemical equilibrium may be written as



where $\nu_i = N_A^\sigma/N_i^\sigma$. This equilibrium can be written in terms of chemical potentials as

$$\mu_i^\alpha + \nu_i \mu_A^{\sigma_A} = \mu_i^{\sigma_A} + \nu_i \mu_A^\alpha$$

This is identical to eq 1.15a.

If it were not for the restrictions of $\sum y_i^{\sigma_A} = 1$ and $\sum y_j^{\sigma_B} = 1$, the equilibrium conditions would be $\mu_i^{\sigma_A} = \mu_A^{\sigma_A}$ and $\mu_j^{\sigma_B} = \mu_B^{\sigma_B}$ for arbitrary components i and j , as is obvious from eq 1.14, like the relation of $\mu_i^\alpha = \mu_i^\beta$ in the equilibrium between bulk phases α and β from $\sum(\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha = 0$ in which there is no restriction of $\sum dn_i^\alpha = 1$ but $dn_i^\alpha = -dn_i^\beta$.

If we assume the equilibrium between the interface and the bulk phases, the well-known Gibbs adsorption equation at $dP = 0$ and $dT = 0$ can be readily derived from eq 1.11 as follows. Namely, if we define Γ_i , $d\mu_i^\sigma$, and $d\mu_i$ as $\Gamma_i \equiv n_i^\sigma/A^\sigma$, $d\mu_i^\sigma \equiv (n_i^{\sigma_A} d\mu_i^{\sigma_A} + n_i^{\sigma_B} d\mu_i^{\sigma_B})/(n_i^{\sigma_A} + n_i^{\sigma_B})$, and $d\mu_i \equiv (n_i^{\sigma_A} d\mu_i^\alpha + n_i^{\sigma_B} d\mu_i^\beta)/(n_i^{\sigma_A} + n_i^{\sigma_B})$, respectively,

$$d\gamma = \sum(\mu_i^\sigma - \mu_i) d\Gamma_i + \sum \Gamma_i (d\mu_i^\sigma - d\mu_i) = -\sum \Gamma_i d\mu_i \quad (1.16)$$

since $\sum(\mu_i^\sigma - \mu_i) d\Gamma_i = 0$, from eq 1.15a,b, and $\sum \Gamma_i d\mu_i^\sigma = 0$ from the Gibbs–Duhem relation in the interface phase. Hence, the Gibbs adsorption equation in eq 1.16 holds under the condition of equilibrium between the interface and bulk phases in eq 1.15a,b. On the other hand, the Gibbs adsorption equation has conventionally been derived from a kind of the Gibbs–Duhem relation applied to eq 1.1 ($S^\sigma dT - V^\sigma dP + A^\sigma d\gamma + \sum n_i^\sigma d\mu_i^{\sigma'} = 0$ with $dT = 0$ and $dP = 0$) and $\mu_i^{\sigma'} = \mu_i$ on the conventional assumption of equilibrium between the interface and bulk phases. However, this derivation is not free from a multitude of mistreatments: e.g., the treatment of γ as a variable independent of the chemical potentials of the interfacial components; the involvement of γ in the Gibbs–Duhem equation for the interface phase which is applicable only to the changes of intensive quantities in the interface phase, despite the fact that γ is a function not only of the chemical potentials of the interfacial molecules but also of those of the bulk molecules; the assumption of the equality of the chemical potentials of each component in the interface and bulk phases at equilibrium. Therefore, the derivation procedure is thermodynamically incorrect, though the result is fortunately correct by virtue of reconciliation among the multiple mistreatments. Incidentally, if one applies a similar Gibbs–Duhem treatment

to the formally correct eq 1.13, one immediately obtains the relation of $A^\sigma d\gamma + \sum n_i^\sigma d\mu_i = 0$. Since originally the Gibbs–Duhem equation must hold unconditionally in a given homogeneous phase regardless of the states of the adjacent phases, the relation of $A^\sigma d\gamma + \sum n_i^\sigma d\mu_i = 0$ must hold without the restriction of equilibrium with bulk phases if the treatment is correct. However, as has been shown in the derivation of eq 1.16, this relation holds only when the system is in an adsorption equilibrium in which the condition of $\sum(\mu_i^\sigma - \mu_i) d\Gamma_i = 0$ is satisfied. This contradiction also stems from the treatment of γ as an independent variable and the involvement of γ , which comprises the variables of the bulk phases, in the Gibbs–Duhem equation for the interface phase. Therefore, the procedure is also incorrect even if applied to the formally correct eq 1.13. It may be readily understood if one considers that what one can obtain from the correct Gibbs–Duhem treatment for interfaces such as liquid–liquid and solid–liquid interfaces at $dT = 0$ is only $\sum \Gamma_i d\mu_i^\sigma = 0$.

The greatest advantage of defining the intrinsic chemical potentials of interfacial components in exactly the same way as those of bulk components may be the fact that γ can be formulated as a function of these chemical potentials, which enables us to describe the dynamic behavior of individual interfacial molecules. From eqs 1.11 and 1.15a,b it follows that

$$\gamma = N_i^\sigma(\mu_i^{\sigma_A} - \mu_i^\alpha) + N_j^\sigma(\mu_j^{\sigma_B} - \mu_j^\beta) \quad (1.17)$$

This is the fundamental equation of γ described as a function of chemical potentials of arbitrary components i and j in the σ_A and σ_B layers of the interfacial double layer and in bulk phases α and β . If we choose the matrix components A and B of phases α and β as i and j , respectively, eq 1.17 can be rewritten as

$$\begin{aligned} \gamma &= N_A^\sigma(\mu_A^{\sigma_A} - \mu_A^\alpha) + N_B^\sigma(\mu_B^{\sigma_B} - \mu_B^\beta) \\ &= \gamma^0 + N_A^\sigma RT \ln \frac{a_A^{\sigma_A}}{a_A^\alpha} + N_B^\sigma RT \ln \frac{a_B^{\sigma_B}}{a_B^\beta} \end{aligned} \quad (1.18)$$

where γ^0 is the specific interfacial energy of phases α and β consisting of pure matrix components A and B, and a represents the activity of each matrix component in the regions indicated by the superscripts.

On the other hand, it follows from eq 1.15a that

$$\left(\frac{a_i^{\sigma_A}}{a_i^\alpha} \right) \left(\frac{a_A^\alpha}{a_A^{\sigma_A}} \right)^{\nu_i} = K_i^\alpha \quad (1.19)$$

where K_i^α is a constant as a function of the standard chemical potentials given by

$$K_i^\alpha \equiv \exp \left[\frac{-(\mu_i^{\Theta, \sigma_A} - \mu_i^{\Theta, \alpha}) + \nu_i(\mu_A^{0, \sigma_A} - \mu_A^{0, \alpha})}{RT} \right] \quad (1.20)$$

with

$$\nu_i \equiv \frac{N_A^\sigma}{N_i^\sigma} \quad (1.21)$$

If the adsorption level is sufficiently low as $\sum x_i^{\sigma_A} \ll 1$, and if

$K_i^\alpha \gg 1$ and $\sum x_i^\alpha \ll 1$, $\sum x_i^{\sigma_A}$ is given by

$$\sum x_i^{\sigma_A} = \frac{\sum K_i^\alpha x_i^\alpha}{1 + \sum K_i^\alpha \nu_i x_i^\alpha} \quad (1.22)$$

and hence, on approximation of $a_A^\alpha = 1$ and $a_B^\beta = 1$, eq 1.5 can be written as a function of x_i^α and x_i^β by

$$\gamma = \gamma^0 + N_A^\sigma RT \ln \left(1 - \frac{\sum K_i^\alpha x_i^\alpha}{1 + \sum K_i^\alpha \nu_i x_i^\alpha} \right) + N_B^\sigma RT \ln \left(1 - \frac{\sum K_i^\beta x_i^\beta}{1 + \sum K_i^\beta \nu_i x_i^\beta} \right) \quad (1.23)$$

where $\nu_i' \equiv N_B^\sigma / N_i^\sigma$. In a special case in which the α phase contains only one nonmatrix component i with matrix component A and the β phase involves only matrix component B , eq 1.22 reduces to

$$x_i^{\sigma_A} = \frac{K_i^\alpha x_i^\alpha}{1 + K_i^\alpha \nu_i x_i^\alpha} \quad (1.24)$$

and eq 1.23 becomes

$$\gamma = \gamma^0 + N_A^\sigma RT \ln \left(1 - \frac{K_i^\alpha x_i^\alpha}{1 + K_i^\alpha \nu_i x_i^\alpha} \right) \quad (1.25)$$

When the adsorption becomes close to the saturation, eq 1.18 with eq 1.19, eq 1.21, $x_i^{\sigma_A} \approx 1$, $a_A^\alpha \approx 1$, and $a_B^{\sigma_A}/a_B^\beta = 1$ yields

$$\gamma = \gamma^0 - N_i^\sigma RT \ln \frac{K_i^\alpha}{f_i^{(1)}} - N_i^\sigma RT \ln a_i^\alpha \quad (1.26)$$

where $f_i^{(1)}$ is the activity coefficient of $x_i^{\sigma_A}$ at $x_i^{\sigma_A} = 1$ and a_i^α is the activity of nonmatrix component i in the bulk of the α phase, which is approximated by x_i^α when $x_i^\alpha \ll 1$. This equation shows that γ is reduced linearly with increasing μ_i^α when the adsorption of nonmatrix component i is close to the saturation, in conformity with eq 1.15a for γ_A .

Furthermore, if $\nu_i = 1$, eqs 1.24 and 1.25 become

$$x_i^{\sigma_A} = \frac{K_i^\alpha x_i^\alpha}{1 + K_i^\alpha x_i^\alpha} \quad (1.27)$$

and

$$\gamma = \gamma^0 - N_i^\sigma RT \ln(1 + K_i^\alpha x_i^\alpha) \quad (1.28)$$

respectively. Equations 1.27 and 1.28 are identical with the well-known Langmuir equation⁴⁻⁶ and Szyszkowski equation,⁷ respectively, and they hold without the restriction of $x_i^{\sigma_A} \ll 1$ because of $\nu_i = 1$ in eq 1.19, as long as the interaction among the adsorbed molecules can be ignored ($f_i = 1$). However, it should be noted that equations 1.21-1.28 have been derived on the assumption of $K_i^\alpha \gg 1$. If this limitation is removed, eqs 1.27 and 1.28 are rewritten from eqs 1.19 and 1.18 in more general forms as

$$x_i^{\sigma_A} = \frac{K_i^\alpha x_i^\alpha}{1 + (K_i^\alpha - 1)x_i^\alpha} \quad (1.29)$$

and

$$\gamma = \gamma^0 - N_i^\sigma RT \ln[1 + (K_i^\alpha - 1)x_i^\alpha] \quad (1.30)$$

As a consequence, the fundamental equation (1.17) involves all elements of the empirically well established Gibbs, Langmuir, and Szyszkowski adsorption equations in the single formula.

In this part 2, the fundamental equation 1.17 will be written in more concrete forms for individual liquid-liquid, solid-liquid, solid-gas, and liquid-gas interfaces under the influence of adsorption, according to the characteristics of these interfaces. Particularly, a new concept of vacancy will be introduced as imaginary matrix molecules of the gas phases of solid-gas and liquid-gas interfaces in order to deal with these interfaces in the same way as the other kinds of interfaces on the basis of the fundamental equation. In this treatment, the vacant space of a gas phase will be assumed to be filled with vacancy molecules of the same distribution in size and shape as that of the real gas molecules in the same gas phase. Also, it will be assumed that pressure as well as temperature is constant in all inhomogeneous systems but solid-gas systems and that the equilibrium constants of adsorption for each component i , K_i^α and K_i^β , are sufficiently greater than unity unless stated otherwise.

2. Interfacial Energies of Different Interfaces

2.1. Liquid-Liquid Interfaces. *Adsorption of Ordinary Molecules.* If we consider an inhomogeneous system consisting of two bulk liquid phases α and β before addition of nonmatrix components, at least either of the interfacial energy components, γ_A^0 and γ_B^0 , must be positive, since $\gamma_A^0 + \gamma_B^0 = \gamma^0 > 0$. However, either γ_A^0 or γ_B^0 can be zero or even negative if the other has a sufficiently high positive value. For instance, if the affinity of matrix molecules A of phase α to matrix molecules B of phase β is greater than that to matrix molecules A themselves, the chemical potential of pure A in the σ_A layer in direct contact with molecules B in the σ_B layer must be lower than that in the bulk of phase α ; i.e., $\mu_A^{0,\sigma_A} < \mu_A^{0,\alpha}$ or $\gamma_A^0 < 0$. In this case, the affinity among molecules B themselves is much greater than their affinity to molecules A to avoid to form a single homogeneous system by mixing together; i.e., $\mu_B^{0,\sigma_B} \gg \mu_B^{0,\beta}$ or $\gamma_B^0 \gg 0$. Such a case may occur in a system consisting of a liquid phase of matrix molecules with a very strong mutual affinity or a very high surface tension, e.g., some organic solvent-mercury systems, in which the organic solvent molecules have a greater affinity to mercury than their own mutual affinity. However, in most cases, both γ_A^0 and γ_B^0 may be positive.

Now let us consider the behavior of the matrix and nonmatrix components in case 1 ($\gamma_A^0 > 0$ and $\gamma_B^0 > 0$) and case 2 ($\gamma_A^0 < 0$ and $\gamma_B^0 > -\gamma_A^0$). For simplicity, we assume that the nonmatrix component is only species i and that $f_i = 1$ $\nu_i = 1$ in eq 1.19. Thus

$$\frac{x_i^{\sigma_A}(1 - x_i^\alpha)}{x_i^\alpha(1 - x_i^{\sigma_A})} = \exp \left[- \frac{(\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha}) - (\mu_A^{0,\sigma_A} - \mu_A^{0,\alpha})}{RT} \right] \equiv K_i^\alpha \quad (2.1)$$

Case 1: $\gamma_A^0 > 0$, $\gamma_B^0 > 0$ ($\mu_A^{0,\sigma_A} - \mu_A^{0,\alpha} > 0$, $\mu_B^{0,\sigma_B} - \mu_B^{0,\beta} > 0$). Here we assume that the affinity of introduced nonmatrix component i to matrix component A of phase α is greater than

to matrix component B of phase β . This may be rephrased that the solubility of component i in solvent A is higher than in solvent B. In this case, $\mu_i^{\Theta,\sigma_A} < \mu_i^{\Theta,\sigma_B} < \mu_i^{\Theta,\beta}$. Since $\mu_i^{\Theta,\sigma_B} < \mu_i^{\Theta,\beta}$ and $\mu_B^{0,\sigma_B} > \mu_B^{0,\beta}$, one finds $K_i^\beta > 1$ from eq 2.1 for the β phase, and thus γ_B is always lowered with increasing x_i^β from eq 1.30 for the β phase unless the solubility of component i in the β phase is negligibly small.

If $\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha} < \mu_A^{0,\sigma_A} - \mu_A^{0,\alpha}$, then $K_i^\alpha > 1$ and thus γ_A is also lowered with increasing x_i^α . As a consequence, γ must be lowered with increasing amount of component i.

If $\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha} = \mu_A^{0,\sigma_A} - \mu_A^{0,\alpha}$, then $K_i^\alpha = 1$ and thus γ_A is kept constant with increasing x_i^α . Hence, the change of γ is equal to the change of γ_B .

If $\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha} > \mu_A^{0,\sigma_A} - \mu_A^{0,\alpha}$, then $K_i^\alpha < 1$ and thus γ_A is rather increased with increasing x_i^α . It is also found from $d\gamma_A = -\sum \Gamma_i^{\sigma_A} d\mu_i^\alpha > 0$ in the Gibbs adsorption equation of eq 1.16, since $\Gamma_A d\mu_A < 0$ and $0 < \Gamma_i d\mu_i < -\Gamma_A d\mu_A$ from eq 1.29 when $K_i^\alpha < 1$. Also, $x_i^\alpha < x_i^\beta$ and $x_A^{\sigma_A} > x_A^\alpha$ at equilibrium, due to the less affinity of component i to matrix B than to matrix A. In this case, the reduction of γ may be lessened by the contribution of the increasing γ_A . However, if the solubility of component i in the β phase is so low that the decrease of γ_B is negligibly small, γ may even increase with increasing x_i^α , though the increase of γ may be rather small due to the small value of $1 - K_i^\alpha$.

Case 2: $\gamma_A^0 < 0$, $\gamma_B^0 > -\gamma_A^0$ ($\mu_A^{0,\sigma_A} - \mu_A^{0,\alpha} < 0$, $\mu_B^{0,\sigma_B} - \mu_B^{0,\beta} > -(\mu_A^{0,\sigma_A} - \mu_A^{0,\alpha})$). Here, we further assume that $\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha} = -(\mu_i^{\Theta,\sigma_B} - \mu_i^{\Theta,\beta})$, as may be valid if the molecule of component i is physically isotropic.

If we assume that the affinity of component i to matrix A is greater than to matrix B like case 1 and thus $\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha} = -(\mu_i^{\Theta,\sigma_B} - \mu_i^{\Theta,\beta}) > 0$, one finds $K_i^\alpha < 1$ from $\mu_i^{\Theta,\sigma_A} > \mu_i^{\Theta,\alpha}$ and $\mu_A^{0,\sigma_A} < \mu_A^{0,\alpha}$ in eq 2.1. Hence γ_A increases with increasing x_i^α . On the other hand, since $\mu_i^{\Theta,\sigma_B} < \mu_i^{\Theta,\beta}$ and $\mu_B^{0,\sigma_B} \gg \mu_B^{0,\beta}$, one finds $K_i^\beta \gg 1$ and thus γ_B decreases with increasing x_i^β . Therefore, if x_i^β is sufficiently high, the change of γ_B may be dominant and hence γ may decrease with decrease of γ_B . However, if $\mu_i^{\Theta,\alpha} \ll \mu_i^{\Theta,\beta}$ so that x_i^β is extremely small, then γ_B is kept constant and thus γ more or less increases with increasing γ_A .

If the affinity of component i to matrix A is less than to matrix B, component i is mainly dissolved in phase β . In this case, one finds $\mu_i^{\Theta,\alpha} > \mu_i^{\Theta,\beta}$ and $\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha} = -(\mu_i^{\Theta,\sigma_B} - \mu_i^{\Theta,\beta}) < 0$. Hence, if $\mu_i^{\Theta,\sigma_B} - \mu_i^{\Theta,\beta} < \mu_B^{0,\sigma_B} - \mu_B^{0,\alpha}$, then $K_i^\beta > 1$ and thus γ_B decreases with an increasing amount of component i, while K_i^α changes from $K_i^\alpha < 1$ to $K_i^\alpha > 1$ with increasing $\mu_i^{\Theta,\sigma_B} - \mu_i^{\Theta,\beta}$ or decreasing $\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha}$. Although γ_A more or less increases with increasing x_i^α when $K_i^\alpha < 1$ ($\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha} > \mu_A^{0,\sigma_A} - \mu_A^{0,\alpha}$) and decreases when $K_i^\alpha > 1$ ($\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha} < \mu_A^{0,\sigma_A} - \mu_A^{0,\alpha}$), γ must always decrease with the decrease of the dominating γ_B since $K_i^\beta > K_i^\alpha$ and $x_i^\beta > x_i^\alpha$. Finally, if $\mu_i^{\Theta,\sigma_B} - \mu_i^{\Theta,\beta}$ becomes so high as $\mu_i^{\Theta,\sigma_B} - \mu_i^{\Theta,\beta} \gg \mu_B^{0,\sigma_B} - \mu_B^{0,\beta}$, then $K_i^\beta \ll 1$, though $K_i^\alpha \gg 1$ since $\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha} = -(\mu_i^{\Theta,\sigma_B} - \mu_i^{\Theta,\beta}) \ll -(\mu_B^{0,\sigma_B} - \mu_B^{0,\beta}) < \mu_A^{0,\sigma_A} - \mu_A^{0,\alpha} < 0$. Thus, if x_i^α is sufficiently high, γ decreases with decreasing γ_A , but if x_i^α is extremely small, γ_A may be kept constant and thus γ may more or less increase with increasing γ_B .

Adsorption of Amphiphilic Molecules. If the solute is an amphiphilic compound, the α -philic and β -philic moieties of each adsorbed amphiphilic molecule must be in the σ_A and σ_B layers, respectively, and behave in couples. Here, we assume that the amphiphilic molecules, pq, are mostly dissolved in the

β phase. In this case, γ is generally given by

$$\gamma = N_A^\sigma(\mu_A^{\sigma_A} - \mu_A^\alpha)y_A^{\sigma_A} + N_B^\sigma(\mu_B^{\sigma_B} - \mu_B^\beta)y_B^{\sigma_B} + N_{pq}^\sigma(\mu_{pq}^{\sigma} - \mu_{pq}^\beta)y_{pq}^\sigma \quad (2.2)$$

where y is the area fraction of each interfacial component, N_{pq}^σ is the two-dimensional maximum molar density of the amphiphile consisting of an α -philic moiety p and β -philic moiety q, and μ_{pq}^β is the chemical potential of the amphiphile in the β phase, which is equal to μ_{pq}^α at equilibrium. Since $dy = 0$ at equilibrium for the change of the area fractions of the interfacial components under the conditions of $dy_A^{\sigma_A} = -dy_p^{\sigma_A}$, $dy_B^{\sigma_B} = -dy_q^{\sigma_B}$, and $N_{pq}^\sigma dy_{pq}^\sigma = N_p^\sigma dy_p^{\sigma_A} = N_q^\sigma dy_q^{\sigma_B}$, one finds the following relationship:

$$\nu_p(\mu_A^{\sigma_A} - \mu_A^\alpha) + \nu_q'(\mu_B^{\sigma_B} - \mu_B^\beta) = \mu_{pq}^\sigma - \mu_{pq}^\beta \quad (2.3)$$

where $\nu_p \equiv N_p^\sigma/N_{pq}^\sigma$ and $\nu_q' \equiv N_q^\sigma/N_{pq}^\sigma$. Inserting this relation into eq 2.2, one obtains

$$\gamma = N_A^\sigma(\mu_A^{\sigma_A} - \mu_A^\alpha) + N_B^\sigma(\mu_B^{\sigma_B} - \mu_B^\beta) \quad (2.4)$$

which is identical with eq 1.18. Also, eq 2.3 gives

$$\frac{a_{pq}^\sigma \left(\frac{a_A^\alpha}{a_A^{\sigma_A}} \right)^{\nu_p} \left(\frac{a_B^\beta}{a_B^{\sigma_B}} \right)^{\nu_q'}}{a_{pq}^\beta \left(\frac{a_A^{\sigma_A}}{a_A^\alpha} \right) \left(\frac{a_B^{\sigma_B}}{a_B^\beta} \right)} = K_{pq}^\beta \quad (2.5)$$

where a_{pq} , a_A , and a_B are the activities of the amphiphilic molecules and matrix molecules A and B, respectively, in the regions designated by the superscripts, and

$$K_{pq}^\beta \equiv \exp \left[\frac{-(\mu_{pq}^{\Theta,\sigma} - \mu_{pq}^{\Theta,\beta}) + \nu_p(\mu_A^{0,\sigma_A} - \mu_A^0) + \nu_q'(\mu_B^{0,\sigma_B} - \mu_B^0)}{RT} \right] \quad (2.6)$$

Now let us consider the following three cases according to the magnitude of the maximum molar density of moiety p, N_p^σ , against that of moiety q, N_q^σ .

Case 1: $N_p^\sigma < N_q^\sigma$ ($N_{pq}^\sigma = N_p^\sigma$, $y_{pq}^\sigma = y_p^{\sigma_A}$, $x_{pq}^\sigma = x_p^{\sigma_A}$). a. $x_p^{\sigma_A} \ll 1$. In the low adsorption range, all activity coefficients of the interfacial components are approximated to be unity, $x_q^{\sigma_B} \approx \nu_B x_p^{\sigma_A}$, $a_{pq}^\beta \approx x_{pq}^\beta$, $a_A^\alpha \approx 1$, and $a_B^\beta \approx 1$, where $x_q^{\sigma_B}$ and $x_p^{\sigma_A}$ are the mole fractions of q and p in the σ_B and σ_A layers, respectively, and $\nu_B \equiv N_A^\sigma/N_B^\sigma$. Thus, it follows from eq 2.5 that

$$\frac{x_p^{\sigma_A}}{(1 - x_p^{\sigma_A})^{\nu_p}(1 - \nu_B x_p^{\sigma_A})^{\nu_q'}} = K_{pq}^\beta x_{pq}^\beta \quad (2.7)$$

Since $x_p^{\sigma_A} \ll 1$ and $\nu_B x_p^{\sigma_A} \ll 1$, $x_p^{\sigma_A}$ is approximated as

$$x_p^{\sigma_A} = \frac{K_{pq}^\beta x_{pq}^\beta}{1 + K_{pq}^\beta(\nu_p + \nu_q)x_{pq}^\beta} \quad (2.8)$$

where $\nu_q \equiv N_q^\sigma/N_{pq}^\sigma$. Also, since it follows from eq 2.4 using $N_B^\sigma RT \ln(1 - \nu_B x_p^{\sigma_A}) = N_A^\sigma RT \ln(1 - \nu_B x_p^{\sigma_A})^{1/\nu_B} \approx N_A^\sigma RT \ln(1 - x_p^{\sigma_A})$ that

$$\gamma = \gamma^0 + 2N_A^\sigma RT \ln(1 - x_p^{\sigma_A}) \approx \gamma^0 - 2\Gamma_{pq} RT \quad (2.9)$$

one obtains γ as a function of x_{pq}^β as

$$\gamma = \gamma^0 + 2N_A^\sigma RT \ln \left[1 - \frac{K_{pq}^\beta x_{pq}^\beta}{1 + K_{pq}^\beta (\nu_p + \nu_q) x_{pq}^\beta} \right] \approx \gamma^0 - \frac{2N_A^\sigma RT K_{pq}^\beta x_{pq}^\beta}{1 + K_{pq}^\beta (\nu_p + \nu_q) x_{pq}^\beta} \quad (2.10)$$

or

$$\frac{RT}{\gamma^0 - \gamma} \approx \frac{1}{2K_{pq}^\beta N_A^\sigma x_{pq}^\beta} + \frac{1}{2} \left(\frac{1}{N_p^\sigma} + \frac{1}{N_q^\sigma} \right) \quad (2.11)$$

b. $x_p^{\sigma_A} \approx 1$. In the saturated adsorption range, $x_B^{\sigma_B} \approx (\nu_p - \nu_q)/(\nu_p - \nu_q + \nu_B)$ at $x_p^{\sigma_A} \approx 1$ so that eq 2.5 may be written as

$$\frac{f_p^{(1)} \left(\frac{a_A^\alpha}{a_A^{\sigma_A}} \right)^{\nu_p} \left[\frac{a_B^\beta}{f_B} \left(\frac{\nu_p - \nu_q + \nu_B}{\nu_p - \nu_q} \right) \right]^{\nu_q'}}{a_{pq}^\beta \left(\frac{a_A^{\sigma_A}}{a_A^\alpha} \right)} = K_{pq}^\beta \quad (2.12)$$

where $f_p^{(1)}$ is the activity coefficient of $x_p^{\sigma_A}$ at $x_p^{\sigma_A} = 1$ and f_B is that of $x_B^{\sigma_B}$ at $x_B^{\sigma_B} = (\nu_p - \nu_q)/(\nu_p - \nu_q + \nu_B)$. From eqs 2.4 and 2.12,

$$\gamma = \gamma^0 - N_B^\sigma \left(1 - \frac{N_p^\sigma}{N_q^\sigma} \right) RT \ln \frac{a_B^\beta \left(\frac{\nu_p - \nu_q + \nu_B}{\nu_p - \nu_q} \right)}{f_B} - N_p^\sigma RT \ln \frac{K_{pq}^\beta}{f_p^{(1)}} - N_p^\sigma RT \ln a_{pq}^\beta \quad (2.13)$$

Since a_B^β can normally be approximated as $a_B^\beta \approx 1$ and $a_{pq}^\beta \approx x_{pq}^\beta$, one obtains N_p^σ from the plot of γ vs $\ln x_{pq}^\beta$ in the saturated adsorption range. In addition, if molecules A in the σ_A layer and molecules B in the σ_B layers are randomly oriented and hence N_A^σ and N_B^σ are given by $N_A^\sigma = \nu_A^{-2/3} N^{-1}$ and $N_B^\sigma = \nu_B^{-2/3} N^{-1}$ (ν = molecular volume; N = Avogadro number), respectively, K_{pq}^β and N_q^σ are also obtained from the reciprocal plot of eq 2.11 in the low adsorption range as $x_p^{\sigma_A} \ll 1$.

Case 2: $N_p^\sigma > N_q^\sigma$ ($N_{pq}^\sigma = N_q^\sigma$; $y_{pq}^\sigma = y_q^{\sigma_B}$; $x_{pq}^\sigma = x_q^{\sigma_B}$). a. $x_q^{\sigma_B} \ll 1$. In this adsorption range, one finds

$$x_q^{\sigma_B} = \frac{K_{pq}^\beta x_{pq}^\beta}{1 + K_{pq}^\beta (\nu_p' + \nu_q') x_{pq}^\beta} \quad (2.14)$$

and

$$\gamma = \gamma^0 + 2N_B^\sigma RT \ln \left[1 - \frac{K_{pq}^\beta x_{pq}^\beta}{1 + K_{pq}^\beta (\nu_p' + \nu_q') x_{pq}^\beta} \right] \quad (2.15)$$

or

$$\frac{RT}{\gamma^0 - \gamma} \approx \frac{1}{2K_{pq}^\beta N_B^\sigma x_{pq}^\beta} + \frac{1}{2} \left(\frac{1}{N_p^\sigma} + \frac{1}{N_q^\sigma} \right) \quad (2.16)$$

b. $x_q^{\sigma_B} \approx 1$.

$$\frac{f_q^{(1)} \left[\frac{a_A^\alpha}{f_A} \left(\frac{\nu_q' - \nu_p' + \nu_A'}{\nu_q' - \nu_p'} \right) \right]^{\nu_p'}}{a_{pq}^\beta \left[\frac{a_B^\beta}{f_B} \left(\frac{\nu_q' - \nu_p'}{\nu_q' - \nu_p'} \right) \right]^{\nu_q'}} = K_{pq}^\beta \quad (2.17)$$

where f_A is the activity coefficient of $x_A^{\sigma_A}$ at $x_A^{\sigma_A} = (\nu_q' - \nu_p')/(\nu_q' - \nu_p' + \nu_A')$

($\nu_q' - \nu_p' + \nu_A'$) or $x_q^{\sigma_B} = 1$, and

$$\gamma = \gamma^0 - N_A^\sigma \left(1 - \frac{N_q^\sigma}{N_p^\sigma} \right) RT \ln \frac{a_A^\alpha}{f_A} \left(\frac{\nu_q' - \nu_p' + \nu_A'}{\nu_q' - \nu_p'} \right) - N_q^\sigma RT \ln \frac{K_{pq}^\beta}{f_q^{(1)}} - N_q^\sigma RT \ln a_{pq}^\beta \quad (2.18)$$

Case 3: $N_p^\sigma = N_q^\sigma$ ($N_{pq}^\sigma = N_p^\sigma = N_q^\sigma$; $y_{pq}^\sigma = y_p^{\sigma_A} = y_q^{\sigma_B}$). In this case, we may choose either $x_p^{\sigma_A}$ or $x_q^{\sigma_B}$ as x_{pq}^σ . If we choose $x_q^{\sigma_B}$ as x_{pq}^σ , $x_q^{\sigma_B}$ and γ are given as follows.

a. $x_q^{\sigma_B} \ll 1$.

$$x_q^{\sigma_B} = \frac{K_{pq}^\beta x_{pq}^\beta}{1 + 2\nu_q' K_{pq}^\beta x_{pq}^\beta} \quad (2.19)$$

and

$$\gamma = \gamma^0 + 2N_B^\sigma RT \ln \left(1 - \frac{K_{pq}^\beta x_{pq}^\beta}{1 + 2K_{pq}^\beta \nu_q' x_{pq}^\beta} \right) \quad (2.20)$$

or

$$\frac{RT}{\gamma^0 - \gamma} \approx \frac{1}{2K_{pq}^\beta N_B^\sigma x_{pq}^\beta} + \frac{1}{N_q^\sigma} \quad (2.21)$$

b. $x_q^{\sigma_B} \approx 1$. From eq 2.3 with $x_A^{\sigma_A} \approx \nu_B x_B^{\sigma_B}$ at $x_B^{\sigma_B} \approx 0$,

$$\frac{f_q^{(1)} \left(\frac{a_A^\alpha}{a_{pq}^\beta \sqrt[3]{\nu_A} \nu_B x_B^{\sigma_B}} \right)^{\nu_p}}{\left(\frac{a_B^\beta}{\sqrt[3]{\nu_B} x_B^{\sigma_B}} \right)^{\nu_q'}} = K_{pq}^\beta \quad (2.22)$$

where $f_A^{(0)}$ and $f_B^{(0)}$ are the activity coefficients of $x_A^{\sigma_A}$ at $x_A^{\sigma_A} = 0$ and $x_B^{\sigma_B}$ at $x_B^{\sigma_B} = 0$, respectively. And

$$\gamma = \gamma^0 - N_q^\sigma RT \ln \frac{K_{pq}^\beta}{f_q^{(1)}} - N_q^\sigma RT \ln a_{pq}^\beta \quad (2.23)$$

2.2. Solid-Liquid Interfaces. Adsorption to Homogeneous Solid Surface. If the α phase is liquid and the β phase is solid, $a_B^{\sigma_B} = x_B^{\sigma_B} = 1$ and $a_B^\beta = x_B^\beta = 1$ in eq 1.18 or $\gamma_B = \gamma_B^0$ so that

$$\gamma = \gamma^0 + N_A^\sigma RT \ln \frac{a_A^{\sigma_A}}{a_A^\alpha} \quad (2.24)$$

In the range of $\sum' x_i^{\sigma_A} \ll 1$, $\sum' x_i^{\sigma_A}$ is given by eq 1.22 and thus

$$\gamma = \gamma^0 + N_A^\sigma RT \ln \left(1 - \frac{\sum' K_i^\alpha x_i^\alpha}{1 + \sum' K_i^\alpha \nu_i x_i^\alpha} \right) \quad (2.25)$$

If the liquid phase α consists of two components, γ as a function of Γ_i for $x_i^{\sigma_A} \ll 1$ is given by

$$\gamma = \gamma^0 + N_A^\sigma RT \ln \left(1 - \frac{\Gamma_i}{N_A^\sigma} \right) \approx \gamma^0 - \Gamma_i RT \quad (2.26)$$

since $x_i^{\sigma_A} \approx \Gamma_i/N_A^\sigma$. From eq 1.25

$$\gamma = \gamma^0 + N_A^\sigma RT \ln \left(1 - \frac{K_i^\alpha x_i^\alpha}{1 + K_i^\alpha \nu_i x_i^\alpha} \right) \approx \gamma^0 - N_A^\sigma RT K_i^\alpha x_i^\alpha \quad (2.27)$$

In the saturated adsorption range ($x_i^{\sigma_A} \approx 1$), γ is given by eq 1.26.

Adsorption to Heterogeneous Solid Surface. If a solid surface has special adsorption sites to which some component is preferentially adsorbed, we may call it a “heterogeneous surface” and the theoretical treatment may be somewhat different from that for “homogeneous surfaces”.

Let us consider a two-component liquid phase consisting of solvent A and solute X_i , in contact with a heterogeneous solid surface with a maximum molar density of the adsorption sites, N_s^σ , where it is assumed that $N_s^\sigma \ll N_i^\sigma, N_A^\sigma$. In addition, we further assume that one site can adsorb only one molecule of A or X_i and that a solute molecule adsorbed to a specific adsorption site does not expel adsorbed solvent molecules on the neighboring specific adsorption sites. In this case, the adsorption of the solute molecules may proceed virtually through two steps: first, the solute is predominantly adsorbed to the adsorption sites with the increasing concentration until the most sites are occupied by the adsorbed solute molecules, and then the adsorption to the remaining homogeneous surface area starts. However, we must also bear in mind that, even in the first step, the adsorption to the remaining area concurrently takes place, though it is quite limited. Hence, there is generally the following relationship between the initial surface concentration of the matrix (or solvent) molecules in the remaining area, Γ_A^0 , and the surface concentrations of the interfacial components during the adsorption process:

$$\Gamma_A^0 = \Gamma_A + \nu_i \Gamma_i + (\nu_i - 1) \Gamma_{i'} \quad (2.28)$$

where the subscripts A and i denote A and X_i in the remaining area, and i' designates X_i on the adsorption sites. For the components on the absorption sites,

$$\Gamma_{A'}^0 = \Gamma_{A'} + \Gamma_{i'} \quad (2.29)$$

where $\Gamma_{A'}$ is the surface concentration of A on the adsorption sites and $\Gamma_{A'}^0$ is its initial value. On the other hand, the interfacial energy of the σ_A layer, γ_A , is generally given by

$$\gamma_A = \Gamma_A(\mu_A^{\sigma_A} - \mu_A^\alpha) + \Gamma_i(\mu_i^{\sigma_A} - \mu_i^\alpha) + \Gamma_{A'}(\mu_{A'}^{\sigma_A} - \mu_{A'}^\alpha) + \Gamma_{i'}(\mu_{i'}^{\sigma_A} - \mu_{i'}^\alpha) \quad (2.30)$$

Since $dG = 0$ or $d\gamma_A = 0$ at equilibrium for the change of each Γ under the conditions of eqs 2.28 and 2.29, one obtains the following relations:

$$\mu_i^{\sigma_A} - \mu_i^\alpha = \nu_i(\mu_A^{\sigma_A} - \mu_A^\alpha) \quad (2.31)$$

and

$$\mu_{i'}^{\sigma_A} - \mu_{i'}^\alpha = (\nu_i - 1)(\mu_A^{\sigma_A} - \mu_A^\alpha) + \mu_{A'}^{\sigma_A} - \mu_{A'}^\alpha \quad (2.32)$$

Substitution of eqs 2.31 and 2.32 into eq 2.30 gives

$$\gamma_A = \Gamma_A^0(\mu_A^{\sigma_A} - \mu_A^\alpha) + \Gamma_{A'}^0(\mu_{A'}^{\sigma_A} - \mu_{A'}^\alpha) \quad (2.33)$$

Since

$$\gamma_A^0 = \Gamma_A^0(\mu_A^{0,\sigma_A} - \mu_A^0) + \Gamma_{A'}^0(\mu_{A'}^{0,\sigma_A} - \mu_{A'}^0) \quad (2.34)$$

and since $\gamma_B = \gamma_B^0$, the total interfacial energy γ is given by

$$\gamma = \gamma^0 + \Gamma_A^0 RT \ln \frac{a_A^\sigma}{a_A^\alpha} + \Gamma_{A'}^0 RT \ln \frac{a_{A'}^\sigma}{a_{A'}^\alpha} \quad (2.35)$$

where $\gamma^0 = \gamma_A^0 + \gamma_B^0$, and $a_A^\sigma, a_{A'}^\sigma$ are the activities of A and A' on the solid surface, respectively. Since the mole fractions of i and i' on the solid surface, x_i^σ and $x_{i'}^\sigma$, are given by

$$x_i^\sigma = \frac{\Gamma_i}{\Gamma_i + \Gamma_A} = \frac{\Gamma_i}{\Gamma_A^0 - (\nu_i - 1)(\Gamma_i + \Gamma_{i'})}; \quad x_{i'}^\sigma = \frac{\Gamma_{i'}}{\Gamma_{A'}^0} \quad (2.36)$$

and since

$$\Gamma_A^0 = N_A^\sigma - N_s^\sigma; \quad \Gamma_{A'}^0 = N_s^\sigma \quad (2.37)$$

Equation 2.35 may be written as

$$\gamma = \gamma^0 + (N_A^\sigma - N_s^\sigma) RT \times \ln \frac{f_A}{a_A^\alpha} \left[1 - \frac{\Gamma_i}{N_A^\sigma - N_s^\sigma - (\nu_i - 1)(\Gamma_i + \Gamma_{i'})} \right] + N_s^\sigma RT \ln \frac{f_{A'}}{a_{A'}^\alpha} \left(1 - \frac{\Gamma_{i'}}{N_s^\sigma} \right) \quad (2.38)$$

where f_A and $f_{A'}$ are the activity coefficients of x_A^σ and $x_{A'}^\sigma$, respectively.

Now let us consider the change of γ in the first and second steps for adsorption in the case of $N_s^\sigma \ll N_i^\sigma, N_A^\sigma$.

a. First Step. During the first step, $x_i^\sigma \ll x_{i'}^\sigma \leq 1$ due to $\mu_{i'}^{\Theta,\sigma_A} < \mu_i^{\Theta,\sigma_A}$, $f_A \approx f_{A'} \approx 1$ due to $\Gamma_i/\Gamma_A^\sigma \ll 1$, and $a_A^\alpha \approx 1$ due to $x_i^\alpha \ll 1$. Thus, eq 2.38 reduces to

$$\gamma = \gamma^0 + N_s^\sigma RT \ln \left(1 - \frac{\Gamma_{i'}}{N_s^\sigma} \right) \quad (2.39)$$

This equation may hold until the end of the first step.

On the other hand, it follows from eq 2.32 that

$$\frac{a_{i'}^\sigma}{a_i^\sigma} \frac{a_A^\alpha}{a_{A'}^\alpha} \left(\frac{a_A^\alpha}{a_{A'}^\alpha} \right)^{\nu_i-1} = K_i^\alpha \quad (2.40)$$

where $a_{i'}^\sigma$ is the activity of i' on the solid surface and

$$K_{i'}^\alpha \equiv \exp \left[\frac{-(\mu_{i'}^{\Theta,\sigma_A} - \mu_i^{\Theta,\sigma_A}) + (\nu_i - 1)(\mu_A^{0,\sigma_A} - \mu_A^0) + (\mu_{A'}^{0,\sigma_A} - \mu_{A'}^0)}{RT} \right] \quad (2.41)$$

During the first step of adsorption, all activities may be approximated by the individual mole fractions and $a_A^\alpha \approx 1$. Hence, the following relation may hold throughout the first step:

$$x_{i'}^\sigma = \frac{\Gamma_{i'}}{N_s^\sigma} = \frac{K_{i'}^\alpha x_i^\alpha}{1 + K_{i'}^\alpha x_i^\alpha} \quad (2.42)$$

Apparently, this equation does not involve ν_i in contrast to eq

1.24 for the homogeneous surface. This is because the maximum surface concentrations of A and X_i adsorbed to the specific sites are both limited to N_s^σ , irrespective of their own N_A^σ and N_i^σ . As a consequence, combination of eqs 2.39 and 2.42 yields

$$\gamma = \gamma^0 - N_s^\sigma RT \ln(1 + K_i^\alpha x_i^\alpha) \quad (2.43)$$

As the specific adsorption sites become saturated with X_i , eq 2.43 is approximated by

$$\gamma = \gamma^0 - N_s^\sigma RT \ln K_i^\alpha x_i^\alpha \quad (2.44)$$

Comparison of eqs 2.43 and 2.44 for a heterogeneous surface with eqs 2.27 and 1.26 for a homogeneous surface shows us that the determinant of γ is always N_s^σ for the former, while it is initially N_A^σ and finally N_i^σ for the latter.

b. Second Step. When the adsorption sites are mostly saturated with X_i , the second step may start. In this stage, $\Gamma_i \approx \Gamma_{A'}^0 = N_s^\sigma$ so that the mole fraction of component i in the remaining homogeneous area, x_i^σ , in eq 2.36 is given by

$$x_i^\sigma = \frac{\Gamma_i}{N_A^\sigma - \nu_i N_s^\sigma - (\nu_i - 1)\Gamma_i} \quad (2.45)$$

Hence, eq 2.38 may be written as

$$\gamma = \gamma^0 + (N_A^\sigma - N_s^\sigma)RT \times \ln \frac{f_A}{a_A^\alpha} \left[1 - \frac{\Gamma_i}{N_A^\sigma - \nu_i N_s^\sigma - (\nu_i - 1)\Gamma_i} \right] + N_s^\sigma RT \ln \frac{f_{A'}}{a_A^\alpha} \left(1 - \frac{\Gamma_i}{N_s^\sigma} \right) \quad (2.46)$$

On the other hand, it follows from eq 2.31 that

$$\frac{a_A^\sigma}{a_A^\alpha} = \left(\frac{a_i^\sigma}{K_i^\alpha a_i^\alpha} \right)^{\frac{1}{\nu_i}} \quad (2.47)$$

where

$$K_i^\alpha \equiv \exp \left[\frac{-(\mu_i^{\Theta, \sigma_A} - \mu_i^{\Theta, \alpha}) + \nu_i(\mu_A^{0, \sigma_A} - \mu_A^{0, \alpha})}{RT} \right] \quad (2.48)$$

Also, from eq 2.40 with $x_i^\sigma \approx 1$ in $a_i^\sigma = f_i x_i^\sigma$ and eq 2.47,

$$\frac{a_{A'}^\sigma}{a_A^\alpha} = \left(\frac{K_i^\alpha a_i^\alpha}{a_i^\sigma} \right)^{\frac{\nu_i - 1}{\nu_i}} \frac{f_{i'}}{K_{i'}^\alpha a_i^\alpha} \quad (2.49)$$

where $f_{i'}$ may change even after the first step ($x_i^\sigma \approx 1$) due to the interaction from the increasing X_i in the homogeneous area. Inserting eqs 2.37, 2.47, and 2.49 into eq 2.35, one obtains

$$\gamma = \gamma^0 - (N_i^\sigma - N_s^\sigma)RT \ln \frac{K_i^\alpha a_i^\alpha}{a_i^\sigma} - N_s^\sigma RT \ln \frac{K_{i'}^\alpha a_i^\alpha}{f_{i'}} \quad (2.50)$$

In the early stage of the second step ($x_i^\sigma \ll 1$), $a_i^\sigma \approx x_i^\sigma$, $a_A^\sigma \approx x_A^\sigma = 1 - x_i^\sigma$, and $a_A^\alpha \approx 1$ in eq 2.47 so that

$$x_i^\sigma = \frac{K_i^\alpha x_i^\alpha}{1 + K_i^\alpha \nu_i x_i^\alpha} \quad (2.51)$$

Substituting eq 2.51 in eq 2.50 with $a_i^\alpha \approx x_i^\alpha$, one obtains

$$\gamma = \gamma^0 - (N_i^\sigma - N_s^\sigma)RT \ln(1 + K_i^\alpha \nu_i x_i^\alpha) - N_s^\sigma RT \ln K_{i'}^\alpha x_i^\alpha \quad (2.52)$$

In the stage of saturated adsorption, $x_i^\sigma \approx 1$ and $a_i^\sigma = f_i^{(1)}$ in eq 2.50, where $f_i^{(1)}$ is the activity coefficient of x_i^σ at $x_i^\sigma = 1$. Thus, it follows from eq 2.50 that

$$\gamma = \gamma^0 - (N_i^\sigma - N_s^\sigma)RT \ln \frac{K_i^\alpha}{f_i^{(1)}} - N_s^\sigma RT \ln \frac{K_{i'}^\alpha}{f_{i'}^{(1)}} - N_s^\sigma RT \ln a_{i'}^\alpha \quad (2.53)$$

where $f_i^{(1)}$ is $f_{i'}$ when $x_i^\sigma \approx 1$ and it may be kept constant against the change of a_i^α in the saturated stage of the second step.

If the affinity of the solute to their adsorbed molecules is much stronger than that to the remaining open space, double-layer adsorption may occur instead as the second step. However, it may have no direct influence on γ in a dilute system as long as the mole fraction of the matrix component in the σ_A layer does not change (see eq 1.18).

In this section, we have previously assumed that a solute molecule adsorbed to a specific adsorption site does not expel adsorbed solvent molecules on the neighboring specific adsorption sites. However, in the case of multidentate adsorption of a solute molecule by which solvent molecules on the neighboring specific adsorption sites are expelled, we must use $x_{A'}^\sigma = (N_s^\sigma - \nu_i \Gamma_i) / [N_s^\sigma + (1 - \nu_i) \Gamma_i]$ in place of $(1 - \Gamma_i / N_s^\sigma)$ in eq 2.39, where $\nu_i = N_s^\sigma / N_i^\sigma$ and $N_i^\sigma < N_s^\sigma < N_A^\sigma$.

Measurement of the Change of γ_{SL} . As is well known, the Young equation for a liquid droplet on a horizontal solid surface is given by

$$\gamma_{SL} = \gamma_{SG} - \gamma_{LG} \cos \theta \quad (2.54)$$

where γ_{SL} , γ_{SG} , and γ_{LG} are the interfacial energies of the solid–liquid, solid–gas, and liquid–gas interfaces, respectively, and θ is the contact angle of the spherical liquid surface at its perimeter against the solid surface. Since γ_{SG} is virtually kept constant by the change of the concentration of the solute in the liquid droplet, $\pi_{SL} (\equiv \gamma_{SL}^0 - \gamma_{SL})$ will be given by

$$\pi_{SL} = \gamma_{LG} \cos \theta - \gamma_{LG}^0 \cos \theta_0 \quad (2.55)$$

where γ_{LS}^0 and γ_{LG}^0 are the initial values of γ_{SL} and γ_{LG} , respectively, and θ_0 is the initial θ . Thus, π_{SL} may be obtained from the measurement of θ and a separate experiment for γ_{LG} .

There are various arguments as to the validity of the Young equation, raised mainly from the standpoints of the microscopic force balance of the interfacial tensions; e.g., uncertainty of the thermodynamic equilibrium as the entire system, need of corrections for the surface roughness, heterogeneity, adsorption effect of the vapor, etc.⁸ However, the relation of eq 2.54 can readily be derived if one sets the differential of the total surface energy to zero for the changes of θ and curvature of the droplet surface, under the conditions of the constant volume of the liquid droplet maintaining the spherical surface and equality of the differential increase of the solid–gas interfacial area to the decrease of the solid–liquid area. In other words, the Gibbs free energy of the system is at the minimum, and thus eq 2.54 is the necessary and sufficient condition of the thermodynamic equilibrium of the entire system if the effect of gravity can be neglected. Besides, the specific interfacial energy γ is defined for a macroscopic unit area so that it is originally a function of

the microscopic surface area and external surface states. Thus, it is rather reasonable to use the equation as it is without any corrections, if only we employ sufficiently small droplets or use the θ values extrapolated to $V = 0$ for the curves of θ as a function of the droplet volume V , in order to avoid the effect of gravity on the spherical contour.

2.3. Solid–Gas Interfaces. Introduction of Vacancy Concept.

In order to deal with interfaces involving a gas phase in consistency with the other kinds of interfaces, it seems necessary to introduce a new concept of vacancy as an imaginary molecule in the gas phase. In a gas phase, there are no matrix molecules like those in the liquid and solid phases. Thus, we assume that the vacant space is filled with vacancy molecules as the matrix of the gas phase. If the α and β phases are a gas and solid phase, respectively, the adsorption and desorption of the gaseous molecules may be expressed by the following formula similar to that of an ordinary chemical reaction:



where X_i^α is a gas molecule in the α phase, VY_B^σ is a pair of a vacancy V and a solid surface element Y_B^σ , $X_iY_B^\sigma$ is a pair of X_i and Y_B^σ , and V^α is a vacancy in the α phase. Equation 2.56 shows that the adsorption of one X_i^α molecule creates one vacancy of the same size in the α phase and that the desorption of a X_i molecule means the adsorption of a vacancy. For the molecules in the σ_A layer, the σ_B layer is a continuous plane so that the surface area of a surface element Y_B^σ must be equal to that of a X_i in the σ_A layer, and thus the area occupied by a vacancy in the σ_A layer must be equal to that of a Y_B^σ or of a X_i molecule. Thus, the size of a vacancy depends on that of the adsorbed species in contrast to a real matrix molecule. In any case, the total molar density of a mixed gas and the vacancy for the whole α phase is kept constant by the exchange of the real gas molecules between the surface and bulk. This is true even if the molar ratio of all real molecules to the vacancies is varied, as long as the molar ratio among the real components is kept constant. Hence,

$$\sum m_i^\infty dy_i + m_v^\infty dy_v = 0 \quad (2.57)$$

where m_i^∞ is the three-dimensional maximum molar density of component i proper to its species, and m_v^∞ is that of the vacancy in the given phase α including its bulk and surface layer; y_i and y_v are the volume fractions of component i and the vacancy for the whole α phase ($y_i = m_i/m_i^\infty$, $y_v = m_v/m_v^\infty$). Integrating eq 2.57 by using the boundary condition $y_v = 1$ at $\sum m_i^\infty y_i = 0$, one finds

$$\sum m_i^\infty y_i + m_v^\infty y_v = m_v^\infty \quad (2.58)$$

Since $\sum y_i + y_v = 1$, one obtains

$$m_v^\infty = \frac{\sum m_i^\infty y_i}{\sum y_i} \quad (2.59)$$

As $y_i/\sum y_i$ is the volume fraction of component i against the total volume fraction of all the real gas molecules, m_v^∞ for the whole α phase is equal to the overall maximum molar density of all real components, m_∞^α , which is the total molar density of the real gas molecules when they are fully packed in the whole space of the α phase including the bulk and surface layer σ_A

without changing their molar ratio, i.e.,

$$m_v^\infty = m_\infty^\alpha = \frac{1}{\sum (x_i/m_i^\infty)} \quad (2.60)$$

where x_i is the overall mole fraction of real component i against the total mole number of the real components in the whole α phase. Thus, m_v^∞ of the α phase, or m_∞^α , is proper to the given α phase and it is constant as long as the molar ratio of each real component in the whole phase α is kept constant, even if the total volume of the α phase is changed. On the other hand, if adsorption occurs, the compositions in the bulk and surface layer σ_A may differ from the overall composition of the α phase. In particular, the composition of the σ_A layer and the average size of the adsorbed molecules therein are expected to be much different from the overall composition and average size of molecules in the α phase as a whole. However, if we define the two-dimensional size of the vacancy in the σ_A layer according to the mole fractions of the adsorbed real components, the total number of the vacancies in the whole α phase must be changed by the adsorption even if the total volume of the α phase is kept constant. Since it is incongruent with the actual adsorption event from a gas phase, the overall mole fractions, x_i , must be used for the definition of the two-dimensional maximum molar density of the vacancies in the σ_A layer, N_v^σ , so that

$$N_v^\sigma = \frac{1}{\sum (x_i/N_i^\sigma)} = \frac{1}{\sum [x_i/(\delta_i^{\sigma_A} m_i^\infty)]} \quad (2.61)$$

where $\delta_i^{\sigma_A}$ is the thickness of component i in the σ_A layer.

The chemical potentials of the vacancies in the σ_A layer and bulk of the α phase are defined as

$$\mu_v^{\sigma_A} = \mu_v^{0,\sigma_A} + RT \ln a_v^{\sigma_A}; \quad \mu_v^\alpha = \mu_v^{0,\alpha} + RT \ln a_v^\alpha \quad (2.62)$$

where $a_v^{\sigma_A}$ and a_v^α are the activities of the vacancies in the surface and bulk zones of the α phase given by

$$a_v^{\sigma_A} = g_v^{\sigma_A} z_v^{\sigma_A}; \quad a_v^\alpha = g_v^\alpha z_v^\alpha \quad (2.63)$$

The $z_v^{\sigma_A}$ and z_v^α are the mole fractions of the vacancies against all components including the vacancy in the surface layer and bulk of the α phase, respectively; i.e.,

$$z_v^{\sigma_A} = \frac{n_v^{\sigma_A}}{\sum^* n_i^{\sigma_A}} = \frac{m_v^{\sigma_A}}{\sum^* m_i^{\sigma_A}}; \quad z_v^\alpha = \frac{n_v^\alpha}{\sum^* n_i^\alpha} = \frac{m_v^\alpha}{\sum^* m_i^\alpha} \quad (2.64)$$

where \sum^* means the summation for all components including the vacancy ($\sum^* n_i = \sum n_i + n_v$); n_i and m_i are the mole number and molar density of component i including the vacancy component, respectively. The g_v is the activity coefficient of z_v . As a consequence, γ_A can be written from eq 2.62 by

$$\gamma_A = \gamma_A^0 + N_v^\sigma RT \ln \frac{a_v^{\sigma_A}}{a_v^\alpha} \quad (2.65)$$

where

$$\gamma_A^0 = N_v^\sigma (\mu_v^{0,\sigma_A} - \mu_v^{0,\alpha}) \quad (2.66)$$

The γ_A^0 means the surface energy of the σ_A layer in the total vacuum, and it must be zero, since originally $\gamma^0 = \gamma_B^0$. Besides, it seems reasonable to assume the chemical potential of the

vacancies in the total vacuum, $\mu_v^{0,\alpha}$, to be zero. Hence, $\mu_v^{0,\sigma_A} = \mu_v^{0,\alpha} = 0$. Therefore, $\mu_v^{\sigma_A}$ and μ_v^α in a gas phase are written as

$$\mu_v^{\sigma_A} = RT \ln a_v^{\sigma_A}; \quad \mu_v^\alpha = RT \ln a_v^\alpha \quad (2.67)$$

Also,

$$\gamma_A = N_v^\sigma RT \ln \frac{a_v^{\sigma_A}}{a_v^\alpha}; \quad \gamma_B = \gamma^0 \quad (2.68)$$

Thus, γ ($=\gamma_A + \gamma_B$) is given by

$$\gamma = \gamma^0 + N_v^\sigma RT \ln \frac{a_v^{\sigma_A}}{a_v^\alpha} \quad (2.69)$$

According to eq 2.67, as the pressure of the α phase increases due to the increase in total molar density of the real gas molecules, a_v^α is lowered below unity so that the negative value of μ_v^α is enlarged. If the real molecules are adsorbed into the σ_A layer, $a_v^{\sigma_A}$ becomes still lower than a_v^α and thus γ_A becomes negative due to the $\mu_v^{\sigma_A}$ lower than μ_v^α . In other words, the pressure in the σ_A layer is expected to be higher than that in the bulk when adsorption occurs. This may be readily understood if one considers that the highly condensed gas molecules on the solid surface must be subject to a higher pressure than those in the dilute gas phase, though the pressure, or the force of their exhalation, in the surface layer is balanced by attraction from the solid surface. The negativity of γ_A must increase with the progress of adsorption but within the limit of $\gamma = \gamma_A + \gamma_B > 0$. If γ_A is excessively lowered as $\gamma = \gamma_A + \gamma_B \leq 0$, and if the surface molecules of the solid are able to rearrange themselves, small particles of the solid will be formed on the solid surface to increase the surface area.

On the other hand, since

$$\gamma_A = N_i^\sigma (\mu_i^{\sigma_A} - \mu_i^\alpha) = N_v^\sigma (\mu_v^{\sigma_A} - \mu_v^\alpha) \quad (2.70)$$

for arbitrary real component i , it follows that

$$\frac{a_i^{\sigma_A}}{a_i^\alpha} \left(\frac{a_v^\alpha}{a_v^{\sigma_A}} \right)^{v_i} = K_i^\alpha \quad (2.71)$$

where

$$K_i^\alpha \equiv \exp \left[\frac{-(\mu_i^{\Theta,\sigma_A} - \mu_i^{\Theta,\alpha})}{RT} \right] \quad (2.72)$$

and

$$v_i \equiv \frac{N_v^\sigma}{N_i^\sigma} \quad (2.73)$$

If $\sum z_i \ll 1$ in both the bulk and surface, it follows from eq 2.71 that

$$\sum z_i^{\sigma_A} = \frac{\sum K_i^\alpha z_i^\alpha}{1 + \sum K_i^\alpha v_i z_i^\alpha} \quad (2.74)$$

Since $a_v^\alpha \approx 1$ and $a_v^{\sigma_A} \approx 1 - \sum z_i^{\sigma_A}$, one obtains from eq 2.69

$$\gamma = \gamma^0 + N_v^\sigma RT \ln \left[1 - \frac{\sum K_i^\alpha z_i^\alpha}{1 + \sum K_i^\alpha v_i z_i^\alpha} \right] \quad (2.75)$$

Equations 2.74 and 2.75 correspond to eqs 1.22 and 1.23, respectively. Here we use \sum in eqs 2.74 and 2.75 instead of \sum' , because \sum' is for all real nonmatrix components in the presence of a *real* matrix component, in contrast to \sum for all real components in general and \sum^* for all components including vacancy. From the assumption of the sufficiently dilute gas phase, each z_i^α is given by

$$z_i^\alpha = \frac{p_i}{m_\infty^\alpha RT} \quad (2.76)$$

where p_i is the partial pressure of component i . Specifically, in a single-component gas phase, $v_i = 1$ from eq 2.73, and hence $z_i^{\sigma_A}$ in the low adsorption range is given by

$$z_i^{\sigma_A} = \frac{K_i^\alpha z_i^\alpha}{1 + K_i^\alpha z_i^\alpha} \quad (2.77)$$

and γ is given by

$$\gamma = \gamma^0 - N_i^\sigma RT \ln(1 + K_i^\alpha z_i^\alpha) = \gamma^0 - N_i^\sigma RT \ln \left(1 + \frac{K_i^\alpha P}{m_i^\infty RT} \right) \quad (2.78)$$

where P is the pressure in the bulk of phase α . And, in the saturated adsorption range γ is given from eqs 2.69 and 2.71 with $z_i^{\sigma_A} = 1$ as

$$\gamma = \gamma^0 - N_i^\sigma RT \ln \frac{K_i^\alpha}{g_i^{(1)}} - N_i^\sigma RT \ln a_i^\alpha \quad (2.79)$$

where $g_i^{(1)}$ is the activity coefficient of $z_i^{\sigma_A}$ at $z_i^{\sigma_A} = 1$. If the gas phase is still sufficiently dilute, $a_i^\alpha = z_i^\alpha = P/m_i^\infty RT$. Therefore, in solid–gas interfaces containing only one gaseous species, the prelogarithm factor is constant ($=N_i^\sigma RT$) for the whole adsorption range in contrast to liquid–liquid and liquid–homogeneous solid interfaces. If the solid surface is heterogeneous ($N_s^\sigma \ll N_i^\sigma$), it follows analogously from eq 2.43 that

$$\gamma = \gamma^0 - N_s^\sigma RT \ln(1 + K_i^\alpha z_i^\alpha) \quad (2.80)$$

which holds throughout the first step of the adsorption.

On the other hand, N_i^σ and K_i^α ($\gg 1$) of pure gas species i are determined by the following reciprocal plot from eq 2.77 in a similar manner to the treatment of eq 2.35 of part 1:

$$\frac{1}{\Gamma_i^{\sigma_A}} = \left(\frac{m_i^\infty}{K_i^\alpha N_i^\sigma} \right) \frac{1}{m_i^\alpha} + \frac{1}{N_i^\sigma} \quad (2.81)$$

If the assumption of $K_i^\alpha \gg 1$ is not allowed, eq 1.29 with x_i replaced by z_i should be used instead of eq 2.81. In this case,

$$\frac{1}{\Gamma_i^{\sigma_A}} = \left(\frac{m_i^\infty}{K_i^\alpha N_i^\sigma} \right) \frac{1}{m_i^\alpha} + \frac{K_i^\alpha - 1}{N_i^\sigma K_i^\alpha} \quad (2.82)$$

In a practical system, it is rather rare to be required to specify the absolute value of m_i^∞ or m_∞^α , since we can usually treat these values as a set in combination with the stability constant of adsorption, as one finds K_i^α/m_i^∞ in eqs 2.78, 2.81, and 2.82, and since we can normally use m_i^α instead of $z_i^\alpha (=m_i^\alpha/m_\infty^\alpha)$. Nevertheless, if it happens to be needed to define m_i^∞ , the method described in the last part of this section may be used for a definition of m_i^∞ (see eq 2.96).

If each m_i^∞ has been determined, the thickness of component i in the σ_A layer, $\delta_i^{\sigma_A}$, can be obtained from $\delta_i^{\sigma_A} = N_i^\sigma/m_i^\infty$, and thus the configuration of the adsorbed molecules can be estimated like the other interfaces of liquid–liquid, solid–liquid, and solid–gas systems. Conversely, if the configuration of the adsorbed molecules i and their molecular length are known, $\delta_i^{\sigma_A}$ may be directly determined. In this case, m_i^∞ can be evaluated from the data of N_i^σ obtained from the reciprocal plot, when the data of m_i^∞ is unavailable.

As is obvious from the above discussion, the chemical potential of vacancies is expected to be an alternate expression of total pressure. Since the change of internal energy U is generally given by

$$dU = T dS - P dV + \sum \mu_i dn_i \quad (2.83)$$

the total pressure P is defined by the decrease of U for the increase of the volume V with S and n_i for all real components kept constant as

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S, n_1, n_2, \dots, n_i, \dots} \quad (2.84)$$

Hence, if we introduce the concept of molecular volume into thermodynamics, the volume change with the fixed number of molecules of each real component corresponds to the volume change of the space filled with vacancies, V_v ; i.e., $dV = dV_v$. Thus, the total internal energy in a uniform system may be written as

$$U = TS - PV_v + \sum n_i d\mu_i \quad (2.85)$$

In the following Gibbs–Duhem relation in this system,

$$SdT - V_v dP + \sum n_i d\mu_i = 0 \quad (2.86)$$

$-V_v dP$ may be replaced by the chemical potential of the vacancies as the definition of $d\mu_v$:

$$-V_v dP = n_v d\mu_v \quad (2.87)$$

where n_v is the number of the vacancies in the system. Integration for this relation, using $n_v/V_v = m_v^\infty$ and the initial condition, $P = \mu_v = 0$ at $z_v = 1$, gives

$$\mu_v = -\frac{P}{m_v^\infty} \quad (2.88)$$

As a consequence, the general Gibbs–Duhem equation including the variation of pressure at $dT = 0$ is

$$\sum^* n_i d\mu_i = 0 \quad (2.89)$$

If we apply this equation to the interface phase ($\sum^* n_i^\sigma d\mu_i^\sigma =$

0), we obtain the general equation of $d\gamma$ at $dT = 0$ but $dP^\sigma \neq 0$ is

$$d\gamma = -\sum^* \Gamma_i d\mu_i \quad (2.90)$$

Here it should be noted that the overall pressure in the interface, P^σ , is generally not equal to the pressure in the bulk phases, though they have conventionally been treated as equal in the equations of the internal energy and Gibbs–Duhem relation for the interface (see eqs 1.1 and 1.2).

For adsorption of strong adsorptives from a dilute gas phase, $d\gamma$ can be approximated by summation only for the real components as

$$d\gamma = -\sum \Gamma_i d\mu_i \quad (2.91)$$

since $\sum \Gamma_i d\mu_i \gg \Gamma_v d\mu_v$.

The concept of vacancy may apply to liquid phases as well, in which z_v is extremely small. In this case, μ_v^α has a high positive standard chemical potential $\mu_v^{\ominus, \alpha}$ in

$$\mu_v^\alpha = \mu_v^{\ominus, \alpha} + RT \ln a_v^\alpha \quad (2.92)$$

to conform the large negative term of $RT \ln a_v^\alpha$ to $\mu_v^\alpha = -P^\alpha/m_v^\infty$ which must be equal to μ_v^β in the adjacent vapor phase β in equilibrium. On the other hand, if $\gamma_A^0 > 0$ before adsorption for the liquid-side surface layer σ_A in a solid–liquid system, then $\mu_v^{0, \sigma_A} > \mu_v^{0, \alpha}$ from eq 2.66 and thus the pressure in the σ_A layer is lower than in the bulk liquid phase α , corresponding to the negative pressure of the surface tension of the liquid-side surface. If some foreign species is adsorbed to such a surface, the pressure in the σ_A layer increases with the decreasing $\mu_v^{\sigma_A}$ and thus the negative pressure of the surface tension is diminished by the increase of the pressure in the surface layer. In other words, the reduction of γ by adsorption is generally due to the greater increase of the overall pressure in the interface than in the bulk phases. Hence, even if the bulk pressure is kept constant, the pressure in the interface cannot be kept constant during adsorption. However, normally $\sum n_i^{\sigma_A} d\mu_i^{\sigma_A} = -n_v^{\sigma_A} d\mu_v^{\sigma_A} = V_v^{\sigma_A} dP^{\sigma_A} \approx 0$ in the Gibbs–Duhem equation for the liquid-side surface layer σ_A at $dT = 0$ due to the extremely small $n_v^{\sigma_A}$ or $V_v^{\sigma_A}$, in contrast to the gas-side surface layer in a solid–gas or liquid–gas system. Therefore, eq 2.91 usually holds for adsorption from a liquid phase at $dT = 0$, regardless of the change of pressure, unless an extremely high external pressure is applied. In addition, if the liquid phase is sufficiently dilute with some solute species to be strongly adsorbed, $d\gamma$ can be approximated by summation only for the solute species or nonmatrix components in eq 2.91.

It is now evident that γ can be expressed in terms of pressures in the interface and bulk phases using eqs 1.17, 2.60, 2.61, and 2.88 as

$$\gamma = \delta_v^{\sigma_A}(P - P^{\sigma_A}) + \delta_v^{\sigma_B}(P - P^{\sigma_B}) \quad (2.93)$$

where P^{σ_A} , P^{σ_B} , and P are the pressures in the σ_A layer, σ_B layer, and bulk phases α and β , respectively; $\delta_v^{\sigma_A}$ and $\delta_v^{\sigma_B}$ are the thicknesses of the vacancies in the σ_A and σ_B layers, respectively, given by

$$\delta_v^{\sigma_A} = \frac{N_v^{\sigma_A}}{m_v^{\infty, \alpha}} = \frac{\sum (x_i^\alpha/m_i^\infty)}{\sum (x_i^\alpha/N_i^{\sigma_A})}; \quad \delta_v^{\sigma_B} = \frac{N_v^{\sigma_B}}{m_v^{\infty, \beta}} = \frac{\sum (x_i^\beta/m_i^\infty)}{\sum (x_i^\beta/N_i^{\sigma_B})} \quad (2.94)$$

Incidentally, there is the following relationship between the chemical potentials of vacancies in adjacent bulk phases α and β in equilibrium:

$$\frac{\mu_v^\alpha}{\mu_v^\beta} = \frac{m_v^{\infty,\beta}}{m_v^{\infty,\alpha}} \quad (2.95)$$

because $P = -m_v^{\infty,\alpha} \mu_v^\alpha = -m_v^{\infty,\beta} \mu_v^\beta$. Equation 2.95 is consistent with the fact that the free energy loss of μ_v^α in the α phase with the transfer of a vacancy from the α phase to β phase is equal to the free energy gain of $(m_v^{\infty,\beta}/m_v^{\infty,\alpha})\mu_v^\beta$ in the β phase at equilibrium, since the volume of one vacancy of the α phase is equal to the total volume of $(m_v^{\infty,\beta}/m_v^{\infty,\alpha})$ vacancies of the β phase.

If the activity of vacancies in a liquid can be approximated by their mole fraction z_v because of its extremely small value, then $dP = -m_v^\infty RT(dz_v/z_v)$ from eq 2.88. In this case, using the molar density of a pure liquid i given by $m_i = m_i^\infty(1 - z_v)$, the maximum molar density $m_i^\infty (= m_v^\infty)$ may be obtained experimentally from the slope of the plot of m_i against $1 - RT(dm_i/dP)$ in

$$m_i = m_i^\infty \left(1 - RT \frac{dm_i}{dP} \right) \quad (2.96)$$

For m_i^∞ of a gaseous species at room temperature, it may be obtained by extrapolation of m_i^∞ values, measured as a function of temperature on a liquidized specimen below the boiling point, to room temperature if their shape and configuration on the solid surface are unknown.

Probably one may have noticed that there are a multitude of empirically known but theoretically unexplained interfacial phenomena governed by interfacial pressure. For complete elucidation of these pressure effects in interfaces and more general physicochemical phenomena relevant to pressure in bulk phases, the concept of vacancy and fundamental equations derived therefrom, such as the general Gibbs–Duhem equation in eq 2.89, are indispensable, as will be shown in detail elsewhere in thermodynamics based on the concept of vacancy.

2.4. Liquid–Gas Interfaces. If one ignores the negligible effect of adsorption of vapor molecules in the gas-side surface layer σ_A on the overall interfacial energy in a pure liquid–vapor system, one may consider $\gamma_A^0 \approx 0$ and thus $\gamma^0 \approx \gamma_B^0$, where γ_A^0 is the specific surface energy of the gas-side surface layer and γ_B^0 is the specific surface energy or surface tension of the liquid phase β . Since $\gamma_B^0 > 0$ in this system, $\mu_v^{\sigma B} > \mu_v^\beta$ or $P^{\sigma B} < P$ and thus the density of the surface layer of the liquid phase must be somewhat lower than that of the bulk liquid.

The original cause of the higher molar density of the surface vacancies or the lower interfacial pressure than in the bulk liquid is the higher standard chemical potential of the surface molecules of the liquid phase than in the bulk. Since the surface density of vacancies as an exceedingly minor component of the liquid phase is completely governed by the interfacial chemical potentials of the real components, we normally need not take into account the direct contribution of the vacancies to the change of the liquid-side surface energy by adsorption of ordinary nonmatrix molecules from the liquid bulk phase in a liquid–gas system, unless an extremely high external pressure is applied. Nevertheless, we must note that the contribution of the vacancies in the gas phase to the change of the gas-side

surface energy of a liquid–gas interface is significant in the case of adsorption of amphiphilic compounds with a bulky lyophobic moiety, even though the ambient pressure is kept constant.

Adsorption of Ordinary Molecules. If the ambient pressure is assumed to be constant, γ_A of gas phase α of a gas–liquid system is kept constant by adsorption of ordinary solute molecules from the bulk of the liquid phase β . In this case, the specific interfacial energy of the liquid–gas interface, γ , may be written from eq 1.18 as

$$\gamma = \gamma^0 + N_B^\sigma RT \ln \frac{a_B^{\sigma B}}{a_B^\beta} \quad (2.97)$$

where a_B is the activity of the solvent of the liquid phase. In the low adsorption range ($\sum x_i^{\sigma B} \ll 1$, $a_B^\beta \approx 1$), eq 2.97 can be approximated by

$$\gamma = \gamma^0 + N_B^\sigma RT \ln(1 - \sum x_i^{\sigma B}) \quad (2.98)$$

In this equation

$$\sum x_i^{\sigma B} = \frac{\sum K_i^\beta x_i^\beta}{1 + \sum K_i^\beta v_i' x_i^\beta} \quad (2.99)$$

where $v_i' \equiv N_B^\sigma/N_i^\sigma$. If the liquid phase contains only one nonmatrix component i , γ in the saturated adsorption range is given by

$$\gamma = \gamma^0 - N_i^\sigma RT \ln \frac{K_i^\beta}{f_i^{(1)}} - N_i^\sigma RT \ln a_i^\beta \quad (2.100)$$

If the liquid phase remains sufficiently dilute, a_i^β may be approximated by x_i^β .

Adsorption of Amphiphilic Molecules. If the liquid phase contains only one kind of amphiphilic compound as the solute, all equations for amphiphilic molecules in section 2.1 for liquid–liquid interfaces are applicable to liquid–gas interfaces as well simply by setting $N_A^\sigma = N_p^\sigma$ or $v_p = 1$ and replacing $x_p^{\sigma A}$ with $z_p^{\sigma A}$, since the matrix component of the gas phase is vacancy.

For the adsorption of amphiphilic molecules into liquid–gas interfaces, Szyszkowski⁷ proposed the following empirical relation between γ and concentration of fatty acids, C :

$$\frac{\gamma}{\gamma^0} = 1 - K_1 \log_{10} \left(1 + \frac{C}{K_2} \right) \quad (2.101)$$

where $\gamma^0 = \gamma$ at $C = 0$; K_1 and K_2 are constants. He found that K_1 was the same around 0.411 for aqueous solutions of all the fatty acids studied such as propionic, butyric, valeric, and caproic acids in each saturated adsorption range. If their hydrocarbon groups lay flat on the water surfaces, their two-dimensional sizes would be much greater than those of their carboxyl groups ($N_p^\sigma \ll N_q^\sigma$) and thus N_p^σ in eq 2.13 would dramatically be varied according to the length of the hydrocarbon group. In view of the constancy of K_1 for all the fatty acids studied, the hydrocarbon chains must have been oriented vertically.⁵ In this case, the surface area occupied by a carboxyl group may be comparable to or somewhat larger than that of a hydrocarbon group. Hence, the γ seems to be given by eq 2.18 with $N_p^\sigma \approx$

N_q^σ or eq 2.23 as

$$\gamma \approx \gamma^0 - N_q^\sigma RT \ln \frac{K_{pq}^\beta}{f_q^{(1)}} x_{pq}^\beta = \gamma^0 - 2.303 N_q^\sigma RT \log_{10} \left(\frac{K_{pq}^\beta V_B}{f_q^{(1)}} \right) C \quad (2.102)$$

where V_B is the molar volume of water ($V_B = 1.80 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$). Since C/K_2 in eq 2.101 is much greater than unity in the saturated adsorption range, the unity as the first term of the antilogarithm can be neglected and thus eq 2.101 formally agrees with eq 2.102, where the contents of K_1 and K_2 are $K_1 = 2.303 N_q^\sigma RT/\gamma^0$ and $K_2 = f_q^{(1)}/(K_{pq}^\beta V_B)$, respectively. In the case of $K_1 = 0.411$ at 293 K, $N_q^\sigma = 5.34 \times 10^{-10} \text{ mol cm}^{-2}$ from $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\gamma^0 = 72.8 \times 10^{-7} \text{ J cm}^{-2}$. Thus, the surface area occupied by a fatty acid molecule at saturation is calculated to be 31 \AA^2 . This value is reasonably close to the values ($\sim 21.5 \text{ \AA}^2$) found for the higher fatty acids by the study of the films on water.⁵ On the other hand, K_2 in eq 2.101 was found to be constant for any one fatty acid, but its value decreased rapidly as the length of the hydrocarbon chain increased; $K_2 = 0.165, 0.051, 0.015$, and $0.0043 \text{ mol dm}^{-3}$ for propionic acid, butyric acid, valeric acid, and caproic acid, respectively.^{5,7} The decrease of K_2 seems to be mainly due to the increase in K_{pq}^β . The corresponding $K_{pq}^\beta/f_q^{(1)}$ values are calculated as $3.37 \times 10^2, 1.09 \times 10^3, 3.70 \times 10^3$, and 1.29×10^4 . If precise data of γ as a function of x_{pq}^β within $K_{pq}^\beta x_{pq}^\beta \ll 1$ become available and if the hydrocarbon chains remain vertically oriented even at the low adsorption level, N_q^σ , K_{pq}^β , and $f_q^{(1)}$ will be determined by eq 2.16 with $N_B^\sigma = \nu_B^{-2/3} N^{-1}$ on the assumption of random orientation of the water molecules in the σ_B layer, where ν_B is the molecular volume of water and N is the Avogadro number.

3. Discussion

In the case of adsorption from a liquid phase to a homogeneous surface, the original Langmuir equation can be applied only when ν_i happens to be close to unity and the interaction among the adsorbed molecules can be ignored. This may be one of the reasons why several different types of adsorption isotherms have been proposed in place of the Langmuir isotherm to explain experimental data deviated from the latter. However, in the case of adsorption of one kind of molecules from a gas phase, ν_i is always equal to unity so that the Langmuir equation can be applied as long as the interaction among the adsorbed molecules is negligible. Here, it seems noteworthy that, originally, Langmuir⁴ derived his equation (see eq 1.27) for the kinetic equilibrium of adsorption and desorption of molecules of one kind in a gas phase, in which there are of course no real matrix molecules to be excluded from the adsorption layer by the adsorption of gas molecules; i.e., $k_a y_i^\sigma (1 - y_i^\sigma) = k_d y_i^\sigma$, where k_a and k_d are the rate constants of adsorption and desorption, respectively, and y_i^σ and y_i^α are the area fraction of the gas molecules on the surface and their volume fraction or concentration in the bulk of the gas phase, respectively. This equation is identical with eq 2.77, since $K_i^\alpha = k_a/k_d$, and $z_i^{\sigma\alpha} = y_i^\sigma$ and $z_i^\alpha = y_i^\alpha$ when $\nu_i = 1$. Hence, it is exactly in accord with the special case of $\nu_i = 1$ for single-component gas phases. It is of interest that an incipient notion of vacant space is already involved in the Langmuir equation as a factor of the adsorption isotherm in the form of $1 - y_i^\sigma$, corresponding to the vacancy

concept of the present theory. However, it should be noted that, in addition to the assumptions of the absence of the interaction of adsorbed molecules and $\nu_i = 1$, assumptions of $K_i^\alpha \gg 1$ and $x_i^\alpha \ll 1$ are also involved in the original Langmuir equation (1.27). Furthermore, ν_i is usually unequal to unity in general multicomponent phases, even if in two-component phases, except for the case of adsorption to the specific adsorption sites of a heterogeneous solid surface (see eq 2.42). Hence, when we use the original Langmuir equation, we must keep the above limitations in mind. Particularly, special attention should be directed to the significant effects of the different molecular size and shape of each component which are reflected to the ν_i value in the adsorption isotherms and formulae of γ , though it has been disregarded in the conventional treatment due to the lack of its theoretical background.

In this context, the Langmuir isotherm equation for the adsorption of solute from a liquid phase to a solid surface is usually derived on the basis of the equilibrium constant of adsorption of the solute and solvent on the specific sites of the solid surface and in the bulk of the liquid phase;⁹ i.e.,

$$K = \frac{x_i^\sigma a_A^\alpha}{x_A^\sigma a_i^\alpha} \quad (3.1)$$

where x_i^σ and a_A^α are the mole fractions of solute i and solvent A on the surface sites; a_i^α and a_A^α are the activities of the solute i and solvent A in the bulk of the liquid phase α . Though in this conventional treatment the heterogeneous and homogeneous solid surfaces have never been strictly distinguished, it is correct as long as the surface molar density of the sites is sufficiently smaller than the two-dimensional maximum molar densities of the solvent and solute (see section 2.2). If we rephrase the equilibrium of adsorption in terms of the chemical potentials of the solute and solvent in the surface layer and bulk of the liquid phase, it naturally follows that

$$\mu_i^{\sigma\alpha} - \mu_i^\alpha = \mu_A^{\sigma\alpha} - \mu_A^\alpha \quad (3.2)$$

where $\sigma\alpha$ and α denote the surface layer and bulk of the liquid phase, respectively. In other words, the chemical potentials of each component in the surface layer and its bulk phase are not equal, but the difference is equal for all components if the size factor can be ignored (see section 3.3 of part 1). However, the formulation of eq 3.2 has never been allowed within the conventional thermodynamics because of the prescription of the uniform chemical potential of each component throughout an inhomogeneous system in equilibrium.

On the other hand, thermodynamic derivation of the Langmuir equation was once attempted on the following redefinition of the chemical potential of component i in the surface or bulk of a two-component phase, within the realm of conventional thermodynamics which prescribes the uniform chemical potential of each component:¹⁰

$$\mu_i = \mu_i^0 + RT \ln \frac{x_i}{1 - x_i} \quad (3.3)$$

Namely, $\mu_i^\sigma = \mu_i^\alpha$ with μ_i^σ and μ_i^α defined by eq 3.3 apparently leads to eq 1.27. This treatment involves an essential alteration of the original definition of chemical potential given by

$$\mu_i = \mu_i^0 + RT \ln x_i \quad (3.4)$$

which was derived from the following general definition of chemical potential, i.e. the change of the Gibbs free energy by the change of unit mole of component i at fixed T , P , and n_j representing the mole numbers of all components except i , as follows:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \quad (3.5)$$

It is obvious from eq 3.5 that the chemical potential of each component in eq 3.4 is defined independently of the chemical potentials of the other components in the given environment, in contrast to eq 3.3 for the nonmatrix component i which involves an entropy factor of the chemical potential of the coexisting matrix component, $-RT \ln(1 - x_i)$, in itself. The modification may have been done considering the exchange of the surface molecules confined in a limited surface area by adsorption, and the idea was applied to the bulk phase as well. The chemical potentials of components are indeed interdependent through the Gibbs–Duhem relation. However, they are interdependent through the number of molecules of each component as an extensive quantity in the Gibbs–Duhem equation, and it does not affect the definition of chemical potential itself as an intensive quantity. Actually, if one uses the redefined chemical potential of eq 3.3, one will find that even a simplest binary liquid system consisting of two components with no molecular interaction at $dP = 0$ and $dT = 0$ does not satisfy the basic Gibbs–Duhem relation. Also, eq 3.3 leads to an unreasonable conclusion that the chemical potential of a pure substance ($x_i = 1$) is infinite. However, these contradictions are no wonder, since the chemical potential is basically a definite intensive quantity in a given system and hence it cannot be freely altered by redefinition. In this sense, the vacancy concept may be indispensable for the systematic understanding of all interfacial phenomena including interfaces with a gas phase, without redefinition of chemical potential.

4. Conclusions

(1) All kinds of interfacial energies in a multicomponent system can be described consistently on the basis of the fundamental equation (1.17) derived in part 1 of this series,¹ by introduction of the novel concept of *vacancy*.

(2) The molecular size and shape of each component as well as the intermolecular affinity are decisive elements in describing the characteristic behavior of the interfacial molecules and their free energies in the different interfaces. The treatment of these elements strongly depends on the nature of each kind of interface.

(3) Though the interfacial energy is always positive to maintain the inhomogeneity of the system, one of the constituent surface energies can be negative. For example, the surface energy of the gas-side surface in a solid–gas interface becomes negative when some adsorption occurs because of the greater negativity of the chemical potential of vacancies at the gas-

side surface layer than in the bulk gas phase, which corresponds to the higher pressure in the gas-side surface layer than in the bulk gas phase. In contrast, the surface energy of the liquid-side surface in a liquid–gas interface is generally positive, corresponding to the negative pressure in the liquid-side surface, which is observed as the surface tension.

(4) It is generally impossible to keep constant the pressure in the interface during adsorption even if the pressure in the bulk phases is kept constant. The increase of the interfacial pressure by adsorption causes the reduction of the interfacial tension or the interfacial energy.

(5) The reduction of interfacial energy of a liquid–liquid or liquid–gas interface by adsorption of amphiphiles is determined by the change of the surface energy of the surface layer occupied by the larger moieties of the amphiphilic molecules in two-dimensional size.

(6) Except for the adsorption to a heterogeneous solid surface, the reduction of the surface energy of a liquid-side surface by adsorption of a nonmatrix component is initially governed by the two-dimensional size of the matrix molecules, but finally by that of the nonmatrix molecules in the saturated adsorption range. However, in the case of the adsorption from a liquid or gas phase to a heterogeneous solid surface with a sufficiently low density of specific adsorption sites, the reduction of the surface energy of the liquid-side or gas-side surface layer is governed only by the surface density of the specific adsorption sites throughout the adsorption process.

(7) The ν_i value ($=N_A^\sigma/N_i^\sigma$) in the surface layer of a single-component gas phase on a homogeneous solid is equal to unity, because the matrix component is the vacancy whose N_v^σ is equal to N_i^σ . Thus, the surface energy of a single-component gas phase is dominated by the two-dimensional size of the real component.

(8) The application of existing Szyszkowski equation is mostly limited to the case in which the Langmuir equation holds. Hence, for application of the Szyszkowski equation to the adsorption to a heterogeneous solid surface, N_i^σ of the adsorbate must be replaced by N_s^σ of the solid surface. However, even if the Langmuir equation fails to hold, the Szyszkowski equation apparently holds in the saturated adsorption range.

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