Interaction between Solute Elements at Any Given Concentration in Homogeneous Multicomponent Solution

By

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The general relationship between activities and activity coefficients based on Raoultian and Henrian reference states at any given concentration was derived from a somewhat different point of view. It was shown that Wagner type theoretical series expansion is valid at any concentrated solution, and that Taylor series expansion using the interaction parameters at constant concentration ratio is also possible. The conversion equations between several kinds of interaction parameters valid at any given concentration in a multicomponent solution were derived by the aid of Gibbs-Duhem equation and Maxwell cross differentials. In a ternary system 1-2-3, the following relations were obtained at any given concentration:

$$\left(\frac{\partial \ln \gamma_2}{\partial N_3}\right)_{N_2} = \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} + \left(\frac{\partial \ln \gamma_1}{\partial N_3}\right)_{N_1},$$

$$\frac{1}{M_2}\left(\frac{\partial \log f_2}{\partial X_3}\right)_{x_2} = \frac{1}{M_3}\left(\frac{\partial \log f_3}{\partial X_2}\right)_{x_3} + \frac{1}{M_1}\left(\frac{\partial \log f_1}{\partial X_3}\right)_{x_1},$$

where γ (or f) is the activity coefficient in mole fraction basis (or in weight percent basis), N (or X) is the mole fraction (or weight percent), M is the atomic weight and the underscript signified the component to be kept constant. It was also shown that $\beta_i^{(j)} = \beta_j^{(i)}$ is valid at the condition $N_i = N_j$, and consequently it follows that $\partial \ln \gamma_1/\partial N_2 = \partial \ln \gamma_2/\partial N_1$ at $N_1 = N_2 = 0.5$ in a binary solution.

1. Introduction

Interaction parameters at constant concentration representing the interactions between solute atoms or molecules are only applicable to the solution in which the concentration of solutes is nearly equal to zero or to the infinitely dilute solution as seen in the definition by C. Wagner.[1]

This is a very important information concerning a solution and F. Neumann and H. Schenck[2] have been more or less successfuly inter-related to the periodic table as seen in the case of the effect of alloying elements

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on the solubility of carbon in liquid iron. These values, however, deviate from the experimental values at a concentrated solution, and therefore, there is some difficulty in the practical application. This difficuly is due to a Taylor series expansion of the logarithm of the activity coefficient at the point where mole fractions of solutes are zero. It is a special case of a Taylor expansion and may well be called mathematically a Maclaurin expansion.

This paper shows that the "original" Taylor series expansion at a point of any given concentration satisfies such a similar formula as derived by C. Wagner. It is also the object of this study to get the relations between several kinds of interaction parameters at any given concentration, and to show that the relations in the infinitely dilute solution can be derived as a special case.

2. Differences between Activity Coefficients according to Selected Reference States, and Definition of Interaction Parameters

2.1. Differences between activity coefficients according to selected reference states

The following three types of reference states of activity are generally used.

1) Raoultian reference state—Let a_i be the activity and N_i the mole fraction of component i respectively. The activity a_i is equal to unity at $N_i=1$. In this case, activity coefficient γ_i is defined as

$$\gamma_i = \frac{a_i}{N_i}. \tag{2-1}$$

This definition has the following meanings in a multicomponent solution.

Though a_i in a k-components solution is expressed as a function of mole fractions of each component, among them there is a condition:

$$\sum_{l=1}^{k} N_l = 1. \tag{2-2}$$

Then a_i forms a curved surface in the k-dimensional space. The ratio of the length from an arbitrary point P on the plane expressed by eq. (2-2) to the intersection point P_a on the a_i surface of the straight line orthogonal to the N_1, $N_2, \cdots, N_k$ axes through P, and the following length from P to the intersection point P_R on the Raoultian plane of this straight line:

$$a_i{}^\circ(R) = N_i, \tag{2-3}$$

is defined as the activity coefficient of component i, i. e.

$$\gamma_i = \frac{a_i}{a_i^\circ(R)} = \frac{a_i}{N_i}. \qquad (2\text{-}4)$$

These relations in a ternary system are shown in Fig. 1.

Relation between the chemical potential μ_i and the activity of component i is shown as follows

$$\mu_i - \mu_i^\circ = RT \ln a_i$$
$$= RT \ln \gamma_i + RT \ln N_i, \qquad (2\text{-}3)$$

where R is the gas constant, T the absolute temperature of the solution and μ_i° the molar free energy of component i in its pure state.
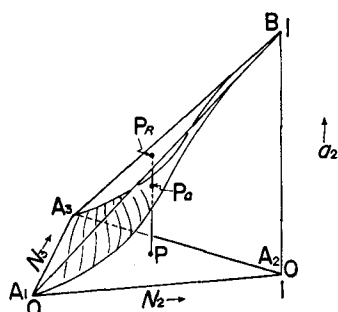

Fig. 1. Schema of the relation between Raoultian activity and mole fractions.

$\Delta A_1A_2A_3$ is mole fractions plane; ΔA_1BA_3 is the plane representing Raoult's law $(a_2^\circ(R)=N_2)$; A_2B is activity axis of the component 2, and curved surface A_1BA_3 hatched in part is activity surface of the component 2 based on Raoultian reference state, respectively. If P_a is the intersection point of the activity surface and the vertical line PP_R at an arbitrary point P on $\Delta A_1A_2A_3$, and P_R is that of the line and Raoult's law plane, the activity coefficient of the component 2 is given by $\gamma_2 = \overline{PP_a}/\overline{PP_R}$.

2) **Henrian reference state on mole fraction basis—Raoultian activity coefficient** has been defined referring to eq. (2-3) which represents Raoult's law in the whole concentration range. In a similar manner, Henrian activity coefficient on mole fraction basis can be defined referring to the plane which represents Henry's law in the whole concentration range. Thus defined Henrian activity on mole fraction basis shows quite similar behaviors which are already known to the infinitely dilute solution, as seen later.

When all of the mole fractions except the components 1 and i are constant (denoting this as subscript N_l; $l \neq 1, i$), let γ_i' be the partial derivative of a_i with respect to N_i at the fixed point Q where only N_i is equal to zero and the others have arbitrary constant values, i. e.

$$\left(\frac{\partial a_i}{\partial N_i}\right)_{N_l\,:\,l \neq 1,\,i} = \gamma_i' \quad \text{at} \quad N_i = 0, \; N_l = N_l^\circ \; (=\text{const}); \; l \neq 1, i, \qquad (2\text{-}6)$$

then the plane representing Henry's law through Q is given by

$$a_i^\circ(H) = \gamma_i' N_i. \qquad (2\text{-}7)$$

Henrian activity coefficient λ_i on mole fraction basis is therefore obtained as

$$\lambda_i = \frac{a_i}{a_i^\circ(H)} = \frac{\gamma_i N_i}{\gamma_i' N_i} = \frac{\gamma_i}{\gamma_i'} \qquad (2\text{-}8)$$

It is practically convenient to use the value γ_i' at $N_i=0$ and $N_l=N_l{}^\circ=0$; $l \neq 1$, i.e. the value at $N_i=0$ in $1-i$ binary system. The form of equation (2-8) holds of course for this case.

The derivative of a_i with respect to N_i at Q, when the ratio of all mole fractions except N_i is kept constant, can be related to γ_i' at constant mole fractions, as follows:

Let n_l be the number of moles of component l ($l=1,2,3,\cdots,k$). Differentiation of some thermodynamic function with respect to n_i has been converted to the differentiation of the function with respect to N_i under the condition of the constant ratio of all mole fractions except N_i.[3] A qualitative explanation concerning this conversion in ternary system is given in Appendix B. Since $\mu_i{}^\circ$ is constant at constant temperature and pressure, the partial differentiation of eq. (2-5) with respect to n_i gives

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{n_l\,:\,l \neq i} = \frac{RT}{a_i}\left(\frac{\partial a_i}{\partial n_i}\right)_{n_l\,:\,l \neq i}$$

$$= \frac{RT}{a_i}\left(\frac{\partial a_i}{\partial N_i}\right)_{N_1/N_2/\cdots/N_{i-1}/N_{i+1}/\cdots/N_k}\left(\frac{\partial N_i}{\partial n_i}\right)_{n_l\,:\,l \neq j}. \qquad (2\text{-}9)$$

Using the relation between number of moles and mole fraction:

$$N_s = \frac{n_s}{\sum\limits_{l=1}^{k} n_l} \qquad (2\text{-}10)$$

following equations are derived

$$\left(\frac{\partial N_s}{\partial n_i}\right)_{n_l\,:\,l \neq i} = -\frac{N_s}{\sum\limits_{l=1}^{k} n_l}, \qquad s \neq i \qquad (2\text{-}11)$$

$$\left(\frac{\partial N_i}{\partial n_i}\right)_{n_l\,:\,l \neq i} = \frac{1-N_i}{\sum\limits_{l=1}^{k} n_l} \qquad (2\text{-}12)$$

Thus eq. (2-9) becomes

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{n_l\,:\,l \neq i} = \frac{RT}{a_i \sum\limits_{l=1}^{k} n_l}(1-N_i)\left(\frac{\partial a_i}{\partial N_i}\right)_{N_1/N_2/\cdots/N_{i-1}/N_{i+1}/\cdots/N_k}, \qquad (1\text{-}13)$$

Since μ_i is a function of mole fractions of each component, the total differential of μ_i is obtained as follows:

$$d\mu_i = \sum_{s=2}^{k}\left(\frac{\partial \mu_i}{\partial N_s}\right)_{N_l\,:\,l \neq 1,\,s} dN_s, \qquad (2\text{-}14)$$

Dividing both sides of this equation with respect to dn_{i_1}

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{n_l \,;\, l \neq i} = \sum_{s=2}^{k} \left(\frac{\partial \mu_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s} \left(\frac{\partial N_s}{\partial n_i}\right)_{n_l \,;\, l \neq i}. \tag{2-15}$$

Substitution of the following equations;

$$\left(\frac{\partial \mu_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s} = \frac{RT}{a_i} \left(\frac{\partial a_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s}, \qquad s \neq 1 \tag{2-16}$$

which is obtained from eq. (2-5), eqs. (2-11) and (2-12) in eq. (2-15) yields

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{n_l \,;\, l \neq i} = \frac{RT}{a_i \sum_{l=2}^{k} n_l} \left[\left(\frac{\partial a_i}{\partial N_i}\right)_{N_l \,;\, l \neq 1, i} - \sum_{s=2}^{k} \left(\frac{\partial a_1}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s} N_s\right]. \tag{2-17}$$

Comparison of eqs. (2-13) and (2-17) leads

$$(1 - N_i)\left(\frac{\partial a_i}{\partial N_i}\right)_{N_1/N_2/\cdots/N_{i-1}/N_{i+1}/\cdots/N_k}$$
$$= \left(\frac{\partial a_i}{\partial N_i}\right)_{N_l \,;\, l \neq 1, i} - \sum_{s=2}^{k} \left(\frac{\partial a_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s} N_s. \tag{2-18}$$

This is a general equation applicable at any given concentration.

As a special case at a point Q where $N_i = 0$, $N_l = N_l°$; $l \neq 1, i$, this equation becomes

$$\left(\frac{\partial a_i}{\partial N_i}\right)_{N_1/N_2/\cdots/N_{i-1}/\cdots/N_{i+1}/\cdots/N_k}$$
$$= \left(\frac{\partial a_i}{\partial N_i}\right)_{N_l \,;\, l \neq 1, s} - \sum_{\substack{s=2 \\ s \neq i}}^{k} \left(\frac{\partial a_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s} N_s°. \tag{2-19}$$

The first term on the right-hand side of eq. (2-19) is equal to γ_i', as shown in eq. (2-6), and considering the following relation derived from eq. (2-4)

$$\left(\frac{\partial a_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s} = N_i \left(\frac{\partial \gamma_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s} + \gamma_i \left(\frac{\partial N_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s}, \tag{2-2-}$$

thus

$$\left(\frac{\partial a_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s} = 0, \qquad \text{at} \quad N_i = 0, \ s \neq i \tag{2-21}$$

is obtained. Then, equation (2-19) is led to

$$\left(\frac{\partial a_i}{\partial N_i}\right)_{N_1/N_2/\cdots/N_{i-1}/N_{i+1}/\cdots/N_k} = \left(\frac{\partial a_i}{\partial N_i}\right)_{N_l \,;\, l \neq 1, i} = \gamma_i' \tag{2-22}$$
$$\text{at} \quad N_i = 0, \ N_l = N_l°; \ l \neq 1, i.$$

Since the Henrian plane through the point Q is also represented by eq. (2-7) for the case of constant mole fraction ratio, the relation of eq. (2-8) is satisfied.

Let $a_i(H)$ be the Henrian activity on mole fraction basis, then

$$a_i(H) = \lambda_i N_i. \tag{2-23}$$

Thus, multipling N_i on both sides of eq. (2-8), one obtains

$$a_i(H) = \frac{a_i}{\gamma_i'}. \tag{2-24}$$

Substitution of eq. (2-24) in eq. (2-5) yields the following relationship between the chemical potential and the Henrian activity $a_i(H)$ on mole fraction basis:

$$
\begin{aligned}
\mu_i - \mu_i^\circ &= RT \ln \gamma_i' + RT \ln a_i(H) \\
&= RT \ln \gamma_i' + RT \ln \lambda_i + RT \ln N_i.
\end{aligned} \tag{2-25}
$$

Now, let us consider the relations between this Henrian activity and the mole fraction of component i in an infinitely dilute solution.

In the infinitely dilute solution of component i, the following equation is valid:

$$\lim_{\substack{N_i \to 0 \\ N_l = N_l^\circ}} \frac{a_i}{N_i} = \lim_{\substack{N_i \to 0 \\ N_l = N_l^\circ}} \left(\frac{\partial a_i}{\partial N_i}\right)_{N_l : l \neq 1, i} = \gamma_i', \tag{2-26}$$

and therefore, from eq. (2-24)

$$\lim_{\substack{N_i \to 0 \\ N_l = N_l^\circ}} \frac{a_i(H)}{N_i} = \lim_{\substack{N_i \to 0 \\ N_l = N_l^\circ}} \frac{a_i}{\gamma_i' N_i} = 1, \tag{2-27}$$

i. e.

$$a_i(H) = N_i \quad \text{in the infinitely dilute solution}$$
$$\text{of component } i. \tag{2-28}$$

Eq. (2-28) means that the value of λ_i is equal to unity in this solution, and the chemical potential μ_i for the infinitely dilute solution can be shown as

$$\mu_i - \mu_i^\circ = RT \ln \gamma_i' = RT \ln N_i. \tag{2-29}$$

3) Henrian reference state on weight percent basis—Activity coefficient f_i can also be determined for this case in quite a similar manner as described above,

a_i is a function of mole fractions of each component, the total differential of a_i can be shown as follows:

$$da_i = \sum_{s=2}^{k} \left(\frac{\partial a_i}{\partial N_s}\right)_{N_l : l \neq 1, s} dN_s. \tag{2-30}$$

Dividing this equation with respect to dX_i, where X_i denotes the weight percent of component i, the following equation is obtained;

$$\left(\frac{\partial a_i}{\partial X_i}\right)_{X_l\,;\,l\,\neq\,1,\,i} = \sum_{r=2}^{k}\left(\frac{\partial a_i}{\partial N_s}\right)_{N_l\,;\,l\,\neq\,1,\,s}\left(\frac{\partial N_s}{\partial X_i}\right)_{X_l\,;\,l\,\neq\,1,\,i} \tag{2-31}$$

Now, there is a general relation between a mole fraction and the weight percent

$$N_s = \cfrac{\cfrac{X_s}{M_s}}{\cfrac{100}{M_1} + \sum\limits_{l=2}^{k}\left(\cfrac{1}{M_l} - \cfrac{1}{M_1}\right)X_l} \tag{2-32}$$

Partial differentiation on both sides of the above equation with respect to X_i yields

$$\left(\frac{\partial N_s}{\partial X_i}\right)_{X_l\,;\,l\,\neq\,1,\,i} = \cfrac{-N_s\left(\cfrac{1}{M_i} - \cfrac{1}{M_1}\right)}{\sum\limits_{l=1}^{k}\cfrac{X_l}{M_l}}\,, \qquad s \neq i \tag{2-33}$$

and

$$\left(\frac{\partial N_i}{\partial X_i}\right)_{X_l\,;\,l\,\neq\,1,\,i} = \cfrac{\cfrac{1}{M_i} - N_i\left(\cfrac{1}{M_i} - \cfrac{1}{M_1}\right)}{\sum\limits_{l=1}^{k}\cfrac{X_l}{M_l}}\,, \tag{2-34}$$

where M_l is the atomic weight of component l. Substitution of eqs. (2-33) and (2-34) in eq. (2-31) gives

$$\left(\frac{\partial a_i}{\partial X_i}\right)_{X_l\,;\,l\,\neq\,1,\,i} = \cfrac{1}{\sum\limits_{l=1}^{k}\cfrac{X_l}{M_l}}\left[\cfrac{1}{M_i}\left(\frac{\partial a_i}{\partial N_i}\right)_{N_l\,;\,l\,\neq\,1,\,i} - \left(\cfrac{1}{M_i} - \cfrac{1}{M_1}\right)\sum\limits_{s=2}^{k}\left(\frac{\partial a_i}{\partial N_s}\right)_{N_l\,;\,l\,\neq\,1,\,s}N_s\right]. \tag{2-35}$$

This relation is applicable at any given concentration.

Let us now consider concerning eq. (2-35) the condition where $N_i = X_i = 0$ and $X_l = X_l{}^\circ$, $N_l = N_l{}^\circ$; $l \neq i$ as described in the preceding section, and by using eqs. (2-6) and (2-21), eq. (2-35) becomes

$$\left(\frac{\partial a_i}{\partial X_i}\right)_{X_l\,;\,l\,\neq\,1,\,i} = \cfrac{\gamma_i{}'}{M_i\sum\limits_{\substack{l=1\\l\neq1}}^{k}\cfrac{X_l{}^\circ}{M_l}} \tag{2-36}$$

Then the plane representing Henry's law is given in Raoultian unit by

$$a_i{}^\circ(\%)(H) = \cfrac{\gamma_i{}'X_i}{M_i\sum\limits_{\substack{l=1\\l\neq i}}^{}\cfrac{X_l{}^\circ}{M_l}} \tag{2-37}$$

The activity coefficient f_i expressed in weight percent basis is, therefore, given as follows:

$$f_i = \cfrac{a_i}{a_i{}^\circ(\%)(H)} = \cfrac{a_iM_i}{\gamma_i{}'X_i}\sum\limits_{\substack{l=1\\l\neq i}}^{k}\cfrac{X_l{}^\circ}{M_l}. \tag{2-38}$$

If the activity in weight percent basis is written as $a_i(\%)$, f_i is defined by the following relation:

$$f_i = \frac{a_i(\%)}{X_i} . \tag{2-39}$$

The conversion equation between a_i and $a_i(\%)$ is then derived from the above two equations, i. e.

$$a_i(\%) = a_i \frac{M_i}{\gamma_i{}'} \sum_{\substack{l=1 \\ l \neq i}}^{k} \frac{X_l{}^{\circ}}{M_l} . \tag{2-40}$$

Although $X_l{}^{\circ}$, $l \neq i$ may not be equal to zero, it will be convenient in practical application to take $X_l{}^{\circ} = 0$, $l \neq 1$. In the latter case, eq. (2-40) becomes

$$a_i(\%) = a_i \frac{100 \, M_i}{\gamma_i{}' M_1} \tag{2-41}$$

Now, let us consider the activity change with respect to X_i, under the condition of constant weight percent ratio except X_i.

The derivative of a_i with respect to X_i under this condition is given by the next equation just as like as eq. (2-9) (see Appendix B).

$$\left(\frac{\partial \mu_i}{\partial n_i} \right)_{n_l \, ; \, l \neq i} = \frac{RT}{a_i} \left(\frac{\partial a_i}{\partial X_i} \right)_{X_1/X_2/\cdots/X_{i-1}/X_{i+1}/\cdots/X_k} \left(\frac{\partial X_i}{\partial n_i} \right)_{n_l \, ; \, l \neq i} . \tag{2-42}$$

From the relation between weight percent and number of moles:

$$X_s = \frac{100 \, M_s n_s}{\sum\limits_{l=1}^{l} M_l n_l} \tag{2-43}$$

following equations are derived:

$$\left(\frac{\partial X_s}{\partial n_i} \right)_{n_l \, ; \, l \neq i} = -X_s \frac{M_i}{\sum\limits_{l=1}^{k} M_l n_l} , \qquad s \neq i \tag{2-44}$$

and

$$\left(\frac{\partial X_i}{\partial n_i} \right)_{n_l \, ; \, l \neq i} = (100 - X_i) \frac{M_i}{\sum\limits_{l=1}^{k} M_l n_l} . \tag{2-45}$$

Substitution of eq. (2-45) in eq. (2-42) gives

$$\left(\frac{\partial \mu_i}{\partial n_i} \right)_{n_l \, ; \, l \neq i} = \frac{M_i RT}{a_i \sum\limits_{l=1}^{k} M_l n_l} (100 - X_i) \left(\frac{\partial a_i}{\partial X_i} \right)_{X_1/X_2/\cdots/X_{i-1}/X_{i+1}/\cdots/X_k} \tag{2-46}$$

On the other hand, the following total differential of μ_i with respect to weight percents:

$$d\mu_i = \sum_{s=2}^{k} \left(\frac{\partial \mu_i}{\partial X_s} \right)_{X_l \, ; \, l \neq 1, s} dX_s , \tag{2-47}$$

yields

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{n_l\,;\,l\neq i} = \sum_{s=2}^{k} \left(\frac{\partial \mu_i}{\partial X_s}\right)_{X_l\,;\,l\neq 1,\,s} \left(\frac{\partial X_s}{\partial n_i}\right)_{n_l\,;\,l\neq i} \tag{2-48}$$

and eq. (2-5) gives

$$\left(\frac{\partial \mu_i}{\partial X_s}\right)_{V_l\,;\,l\neq 1,\,s} = \frac{RT}{a_i} \left(\frac{\partial a_i}{\partial X_s}\right)_{X_l\,;\,l\neq 1,\,s}. \tag{2-49}$$

Substitution of this relation and eqs. (2-44) and (2-45) in eq. (2-48) yields

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{n_l\,;\,l\neq i} = \frac{M_i RT}{a_i \sum_{l=1}^{k} M_l n_l}\left[100\left(\frac{\partial a_i}{\partial X_i}\right)_{X_l\,;\,l\neq 1,\,i} - \sum_{s-2}^{k}\left(\frac{\partial a_i}{\partial X_s}\right)_{X_l\,;\,l\neq 1,\,s} X_s\right]. \tag{2-50}$$

Comparison of eqs. (2-46) and (2-50) results

$$(100-X_i)\left(\frac{\partial a_i}{\partial X_i}\right)_{X_1/X_2/\cdots/X_{i-1}/X_{i+1}/\cdots/X_k}$$
$$= 100\left(\frac{\partial a_i}{\partial X_i}\right)_{X_l\,;\,l\neq 1,\,i} - \sum_{s=2}^{k}\left(\frac{\partial a_i}{\partial X_s}\right)_{X_l\,;\,l\neq 1,\,s} X_s. \tag{2-51}$$

This equation is likely valid as eq. (2-18), at any given concentration.

Now, as the special case for $X_i=0$, $X_l=X_l°$; $l\neq i$,

$$\left(\frac{\partial a_i}{\partial X_s}\right)_{X_l\,;\,l\neq 1,\,s} = 0, \quad \text{at} \quad X_i=0 \tag{2-52}$$

is proved quite as similar as for the case of eq. (2-21), and therefore, eq. (2-51) gives the following relation:

$$\left(\frac{\partial a_i}{\partial X_i}\right)_{X_1/X_2/\cdots/X_{i-1}/X_{i+1}/\cdots/X_k} = \left(\frac{\partial a_i}{\partial X_i}\right)_{X_l\,;\,l\neq 1,\,i} = \frac{r_i'}{M_i \displaystyle\sum_{\substack{l=1 \\ l\neq 1}} \frac{X_l°}{M_l}}. \tag{2-53}$$

In other words, Henrian plane for the case of constant weight percent ratio is also represented by eq. (2-37), and then eqs. (2-40) and (2-41) are also valid for this case.

The relationship between chemical potential μ_i and activity $a_i(\%)$ can be derived from eq. (2-5) by using eq. (2-40) or (2-41), i. e.

$$\mu_i-\mu_i° = RT\ln a_i(\%) - RT\ln \frac{M_i}{r_i'} \sum_{\substack{l=1 \\ l\neq i}}^{k} \frac{X_l°}{M_l}$$
$$= RT\ln f_i + RT\ln X_i - RT\ln \frac{M_i}{r_i'} \sum_{\substack{l=1 \\ l\neq i}}^{k} \frac{X_l°}{M_l} \tag{2-54}$$

or

$$\mu_i - \mu_i{}^\circ = RT \ln a_i(\%) + RT \ln \frac{\gamma_i' M_1}{100\, M_i}$$

$$= RT \ln f_i + RT \ln X_i + RT \ln \frac{\gamma_i' M_1}{100\, M_i} \qquad (2\text{-}55)$$

We can derive all of the relation previously obtained concerning the infinitely dilute solution from preceding equations. In the infinitely dilute solution of X_i, we have got from eq. (2-36)

$$\lim_{\substack{X_i \to 0 \\ X_l = X_l{}^\circ}} \frac{a_i}{X_i} = \lim_{\substack{X_i \to 0 \\ X_l = X_l{}^\circ}} \left(\frac{\partial a_i}{\partial X_i}\right)_{X_l\,;\,l \neq 1,\,i} = \frac{\gamma_i'}{M_i \sum\limits_{\substack{l=1 \\ l \neq i}} \dfrac{X_l{}^\circ}{M_l}} \qquad (2\text{-}56)$$

then from eq. (2-40)

$$\lim_{\substack{X_i \to 0 \\ X_l = X_{l_0}}} \frac{a_i(\%)}{X_i} = \lim_{\substack{X_i \to 0 \\ X_l = X_{l_0}}} \frac{a_i M_i}{X_i \gamma_i'} \sum_{\substack{l=1 \\ l \neq i}}^{k} \frac{X_l{}^\circ}{M_.} = 1 \qquad (2\text{-}57)$$

is obtained. Thus in the infinitely dilute solution of X_i, next relation results

$$a_i(\%) = X_i, \qquad (2\text{-}58)$$

or

$$X_i = \frac{a_i M_i}{\gamma_i'} \sum_{\substack{l=1 \\ l \neq i}}^{k} \frac{X_l{}^\circ}{M_l} \qquad (2\text{-}59)$$
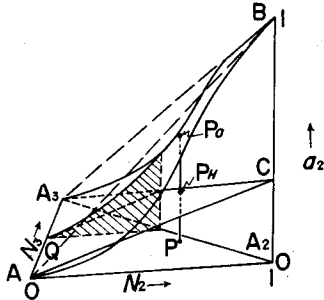

Fig. 2. Schematic representation of the activity coefficient in mole fraction unit based on Henrian reference state.

$\Delta A_1 C A_3$ represents Henry's law plane given by $a_2{}^\circ(H) = \gamma_2' N_2$, where γ_2' is the tangent of activity curve QS of component 2 at the point Q ($N_2{}^\circ = 0$). Then $\overline{PP_H}$ is equal to $\gamma_2' N_2$, and λ_2 is given as the ratio PP_a/PP_H.
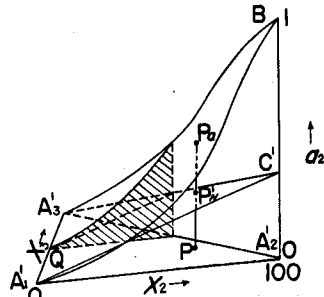
Fig. 3. Schema of the relation between Raoultian activity and weight percents.

$\Delta A_1' A_2' A_3'$ is the weight percent plane. Though $\Delta A_1' C' A_3'$ corresponds to $\Delta A_1 C A_3$ in Fig. 2, it's equation is represented by $a_2{}^\circ(\%)(H) = \gamma_2' X_2 / \{M_2(X_1{}^\circ/M_1 + X_3{}^\circ/M_3)\}$, where $X_1{}^\circ + X_3{}^\circ = 100$, because this Henrian plane is related to weight percent. Hence, Henrian activity coefficient f_2 related to weight percent is given by $f_2 = \overline{PP_a}/\overline{PP_{H'}}$.

In other words, f_i becomes unity from eq. (2-38) or (2-39) in this case, and the relationship between chemical potential and weight percent in this case is shown as the following from eq. (2-54):

$$\mu_i - \mu_i^\circ = RT \ln X_i - RT \ln \frac{M_i}{r_i'} \sum_{\substack{l=1 \\ l \neq i}}^{k} \frac{X_i^\circ}{M_.}$$

(2-60)

or, similarly from eq. (2-55):

$$\mu_i - \mu_i^\circ = RT \ln X_i + RT \ln \frac{r_i' M_1}{100 \, M_i}$$

(2-61)

Fig. 2 and 3 show the graphical relationship between Raoultian and Henrian activity discussed in section 2) and 3), and explain the way to determine the activity coefficient in each ternary system.

2.2. Definition of interaction parameters

There are several kinds of interaction parameters which represent the characteristic effect of added solute element j on thc activity coefficient of a solute element i. These are classified as

1) the interaction parameter of i at constant concentration except that of component 1 and j; i.e.

$$\left(\frac{\partial \ln r_i}{\partial N_j} \right)_{N_l; l \neq 1, j}$$

(2-62)

or

$$\left(\frac{\partial \log f_i}{\partial X_j} \right)_{X_l; l \neq 1, j}$$

(2-63)

which may be called as "interaction parameter at constant mole fraction" or "interaction parameter at constant weight percent",

2) the interaction parameter of i at constant concentration ratio except that of component j, i.e.

$$\left(\frac{\partial \ln r_i}{\partial N_j} \right)_{N_1/N_2/\cdots/N_{j-1}/N_{j+1}/\cdots/N_k} \equiv \beta_i^{(j)}$$

(2-64)

or

$$\left(\frac{\partial \log f_i}{\partial X_j} \right)_{X_1/X_2/\cdots/X_{j-1}/X_{j+1}/\cdots/X_k} \equiv b_i^{(j)}$$

(2-65)

which may be called as "interaction parameter at constant mole fraction ratio" or simply as β, or "interaction parameter at constant weight percent ratio" or simply as b, and this concept had been originally introduccd by N. A. Gokcen.[4] and general relation between β and other parameters have been derived by H. Schenck, W. G. Frohberg and E. Steinmets[3], and

3) the interaction parameter at constant activity of component i, i.e.

$$\left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{a_i} = \varepsilon_i^{(j)}a \qquad (2\text{-}66)$$

or

$$\left(\frac{\partial \log f_i}{\partial X_j}\right)_{a_i} = e_i^{(j)}a \qquad (2\text{-}67)$$

which may be called as "interaction parameter at constant activity"*.

The following derivative:

$$\left(\frac{\partial N_i}{\partial N_j}\right)_{a_i} = m_i^{(j)} \qquad (2\text{-}68)$$

or

$$\left(\frac{\partial X_i}{\partial X_j}\right)_{a_i} = m'_i^{(j)} \qquad (2\text{-}69)$$

which also means a kind of the interaction parameter at constant activity of i, may be called as "solubility parameter".[7]

3. Relationship between Activity Coefficients and Interaction Parameters (Using Taylor Series Expansion)

Activity coefficient γ_i in k-component solution is a function of mole fractions $N_1, N_2, \cdots, N_k$. However, since there is a relation of eq. (2-2) among these mole fractions, the independent variables are reduced to $k-1$, e.g. $N_2, N_3, \cdots, N_k$, Let us show it as $\gamma_i(N_2, N_3, \cdots, N_k)$.

A Taylor series expansion of $\ln \gamma_i$ with respect to mole fractions at a fixed point $(N_2°, N_3°, \cdots, N_k°)$ given the following equation:

$$\ln \gamma_i(N_2, N_3, \cdots, N_k) = \ln \gamma_i(N_2°, N_3°, \cdots, N_k°)$$
$$+ (N_2 - N_2°)\left[\frac{\partial \ln \gamma_i(N_2°, N_3°, \cdots, N_k°)}{\partial N_2}\right]_{N_l; l \neq 1, 2}$$
$$+ (N_3 - N_3°)\left[\frac{\partial \ln \gamma_i(N_2°, N_3°, \cdots, N_k°)}{\partial N_3}\right]_{N_l; l \neq 1, 3}$$
$$+ \cdots$$
$$+ (N_i - N_i°)\left[\frac{\partial \ln \gamma_i(N_2°, N_3°, \cdots, N_k°)}{\partial N_i}\right]_{N_l; l \neq 1, i}$$
$$+ \cdots$$
$$+ (N_j - N_j°)\left[\frac{\partial \ln \gamma_i(N_2°, N_3°, \cdots, N_k°)}{\partial N_j}\right]_{N_l; l \neq 1, j}$$
$$+ \cdots$$
$$+ \frac{1}{2!}\left[\sum_{l=2}^{k}(N_l - N_l°)\frac{\partial}{\partial N_l}\right]^2 \ln \gamma_i + \cdots \qquad (3\text{-}1)$$

---

* Schenck et al[3] used the symbols $\omega_i^{(j)}$ and $o_i^{(j)}$ respectively instead of $\varepsilon_i^{(j)}a$ and $e_i^{(j)}a$, but the authors prefer the latter symbols.

If $|N_l - N_l°| \ll 1$, terms involving second and higher derivatives can be disregarded, and the logarithm of the activity coefficient becomes a linear function:

$$\ln \gamma_i(N_2, N_3, \cdots, N_{i-1}, N_i, N_{i+1}, \cdots, N_{j-1}, N_j, N_{j+1}, \cdots, N_k)$$
$$= \ln \gamma_i(N_2°, N_3°, \cdots, N_k°)$$
$$+ (N_2 - N_2°)\left[\frac{\partial \ln \gamma_i(N_2°, N_3°, \cdots, N_k°)}{\partial N_2}\right]_{N_l; l \neq 1, 2}$$
$$+ \cdots$$
$$+ (N_i - N_i°)\left[\frac{\partial \ln \gamma_i(N_2°, N_3°, \cdots, N_k°)}{\partial N_i}\right]_{N_l; l \neq 1, i}$$
$$+ \cdots$$
$$+ (N_j - N_j°)\left[\frac{\partial \ln \gamma_i(N_2°, N_3°, \cdots, N_k°)}{\partial N_j}\right]_{N_l; l \neq 1, j}$$
$$+ \cdots . \tag{3-2}$$

When all of the mole fractions except N_i and N_1 are kept constant; $N_2°, N_3°, \cdots, N_k°$ (denoting this as $N_l = N_l°$; $l \neq 1, i$), eq. (3-2) gives

$$\ln \gamma_i(N_2°, N_3°, \cdots, N_{i-1}°, N_i, N_{i+1}°, \cdots, N_k°) - \ln \gamma_i°$$
$$= (N_i - N_i°)\left[\frac{\partial \ln \gamma_i(N_2°, N_3°, \cdots, N_k°)}{\partial N_i}\right]_{N_l; l \neq 1, i}, \tag{3-3}$$

where

$$\gamma_i° = \gamma_i(N_2°, N_3°, \cdots, N_k°). \tag{3-4}$$

and similarly

$$\ln \gamma_i(N_2°, N_3°, \cdots, N_{j-1}°, N_j, N_{j+1}°, \cdots, N_k°) - \ln \gamma_i°$$
$$= (N_j - N_j°)\left[\frac{\partial \ln \gamma_i(N_2°, N_3°, \cdots, N_k°)}{\partial N_j}\right]_{N_l; l \neq 1, j} \tag{3-5}$$

for the case $N_l = N_l°$; $l \neq 1, j$.

Using eqs. (3-3) and (3-5), eq. (3-2) can be rewritten as

$$\ln \gamma_i(N_2, N_3, \cdots, N_i, \cdots, N_j, \cdots, N_k)$$
$$= \ln \gamma_i°$$
$$+ \ln \frac{\gamma_i(N_2, N_3°, \cdots, N_k°)}{\gamma_i°}$$
$$+ \ln \frac{\gamma_i(N_2°, N_3, N_4°, \cdots, N_k°)}{\gamma_i°} + \cdots$$
$$+ \ln \frac{\gamma_i(N_2°, \cdots, N_{i-1}°, N_i, N_{i+1}°, \cdots, N_k°)}{\gamma_i°} + \cdots$$
$$+ \ln \frac{\gamma_i(N_2°, \cdots, N_{j-1}°, N_j, N_{j+1}°, \cdots, N_k°)}{\gamma_i°} + \cdots . \tag{3-6}$$

The first and the i-th terms on the right-hand side of this equation may be lumped together. And introduction of Wagner's representation:

$$r_i^{(j)} = \frac{r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_{j-1}^\circ, N_j, N_{j+1}^\circ, \cdots, N_k{}^\circ)}{r_i{}^\circ}, \qquad j \neq i \tag{3-7}$$

to eq. (3-6) yields

$$\ln r_i = \ln r_i^{(2)} + \ln r_i^{(3)} + \cdots + \ln r_i^{(t)} + \cdots + \ln r_i^{(j)} + \cdots + \ln r_i^{(k)}, \tag{3-8}$$

or

$$r_i = r_i^{(2)} r_i^{(3)} \cdots r_i^{(t)} \cdots r_i^{(j)} \cdots r_i^{(k)}, \tag{3-9}$$

where

$$r_i^{(t)} = r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_{i-1}^\circ, N_i, N_{i+1}^\circ, \cdots, N_k{}^\circ). \tag{3-10}$$

Eq. (3-2), for $N_l = N_l{}^\circ$; $l \neq i, j$, takes the following form :

$$\ln r_i(N_2{}^\circ, \cdots, N_{i-1}^\circ, N_i, N_{i+1}^\circ, \cdots, N_{j-1}^\circ, N_j, N_{j+1}^\circ, \cdots, N_k{}^\circ)$$
$$= \ln r_i{}^\circ$$
$$+ (N_i - N_i{}^\circ)\left[\frac{\partial \ln r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_k{}^\circ)}{\partial N_i}\right]_{N_l : l \neq 1, i}$$
$$+ (N_j - N_j{}^\circ)\left[\frac{\partial \ln r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_k{}^\circ)}{\partial N_j}\right]_{N_l : l \neq 1, j}. \tag{3-11}$$

This relation may be rewritten as

$$\ln \frac{r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_{i-1}^\circ, N_i, N_{i+1}^\circ, \cdots, N_{j-1}^\circ, N_j, N_{j+1}^\circ, \cdots, N_k{}^\circ)}{r_i{}^\circ}$$
$$- (N_i - N_i{}^\circ)\left[\frac{\partial \ln r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_k{}^\circ)}{\partial N_i}\right]_{N_l : l \neq 1, i}$$
$$= (N_j - N_j{}^\circ)\left[\frac{\partial \ln r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_k{}^\circ)}{\partial N_j}\right]_{N_l : l \neq 1, j}. \tag{3-12}$$

Then, substitution of eq. (3-5) in this equation gives

$$\ln \frac{r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_{i-1}^\circ, N_i, N_{i+1}^\circ, \cdots, N_{j-1}^\circ, N_j, N_{j+1}^\circ, \cdots, N_k{}^\circ)}{r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_{i-1}^\circ, N_i, N_{i+1}^\circ, \cdots, N_{j-1}^\circ, N_j{}^\circ, N_{j+1}^\circ, \cdots N_k{}^\circ)}$$
$$= (N_j - N_j{}^\circ)\left[\frac{\partial \ln r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_k{}^\circ)}{\partial N_j}\right]_{N_l : l \neq 1, j}. \tag{3-13}$$

The right-hand sides of eqs. (3-5) and (3-13) are identical, thus, using eq. (3-7),

$$r_i^{(j)} = \frac{r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_{i-1}^\circ, N_i, N_{i+1}^\circ, \cdots, N_{j-1}^\circ, N_j, N_{j+1}^\circ, \cdots, N_k{}^\circ)}{r_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_{i-1}^\circ, N_i, N_{i+1}^\circ, \cdots, N_{j-1}^\circ, N_j{}^\circ, N_{j+1}^\circ, \cdots, N_k{}^\circ)} \tag{3-14}$$

It is clear that the substitution of $N_l{}^\circ = 0$; $l \neq i$ in these relations leads to the equations derived by Wagner. That is to say, the relationship derived by Wagner can be expanded to any given concentration. Though some of these have been already derived by K. Niwa and N. Shimozi,[5] and T. Mori,[6] the authors showed these relationship using strictly defined symbols. The reason why we do not use the symbol $\varepsilon_i^{(j)}$ as the interaction parameter as

constant concentration:

$$\left[\frac{\partial \ln \gamma_i(N_2{}^\circ, N_3{}^\circ, \cdots, N_k{}^\circ)}{\partial N_j}\right]_{N_l \,;\, l \neq 1,\, j} = \varepsilon_i^{(j)} \tag{3-15}$$

will be discussed in Appendix A.

It can be readily shown that substitution of λ_i instead of γ_i yields the relations between Henrian activity coefficient on mole fraction basis and its interaction coefficients or interaction parameters, and that of f_i, X_i and log instead of γ_i, N_i and ln, on weight percent basis.

Now, let us consider the relationship between γ_i and the number of moles of each component. Activity coefficient γ_i may be generally regarded as a function of the number of moles $n_1, n_2, \cdots, n_k$. Since $n_1, n_2, \cdots, n_k$ are independent variables, the Taylor series expansion like eq. (3-2) with respect to number of moles includes the term $\gamma_i^{(1)}$ in the equation corresponding to eq. (3-9).

The main important relations of those corresponding to eqs. (3-6), (3-7), (3-9), (3-13) and (3-14) are as follows:

$$\ln \gamma_i(n_1, n_2, \cdots, n_i, \cdots, n_j, \cdots, n_k)$$
$$= \ln \gamma_i{}^\circ$$
$$+ \ln \frac{\gamma_i(n_1, n_2{}^\circ, \cdots, n_k{}^\circ)}{\gamma_i{}^\circ}$$
$$+ \ln \frac{\gamma_i(n_1{}^\circ, n_2, n_3{}^\circ, \cdots, n_k{}^\circ)}{\gamma_i{}^\circ} + \cdots$$
$$+ \ln \frac{\gamma_i(n_1{}^\circ, \cdots, n_{i-1}^\circ, n_i, n_{i+1}^\circ, \cdots, n_k{}^\circ)}{\gamma_i{}^\circ} + \cdots$$
$$+ \ln \frac{\gamma_i(n_1{}^\circ, \cdots, n_{j-1}^\circ, n_j, n_{j+1}^\circ, \cdots, n_k{}^\circ)}{\gamma_i{}^\circ} + \cdots, \tag{3-16}$$

where

$$\gamma_i{}^\circ = \gamma_i(n_1{}^\circ, n_2{}^\circ, \cdots, n_k{}^\circ). \tag{3-17}$$

$$\gamma_i^{(j)} = \frac{\gamma_i(n_1{}^\circ, n_2{}^\circ, \cdots, n_{j-1}^\circ, n_j, n_{j+1}^\circ, \cdots, n_k{}^\circ)}{\gamma_i{}^\circ}, \qquad j \neq i \tag{3-18}$$

$$\gamma i = \gamma_i^{(1)} \gamma_i^{(2)} \gamma_i^{(3)} \cdots \gamma_i^{(i)} \cdots \gamma_i^{(j)} \cdots \gamma_i^{(k)}, \tag{3-19}$$

where only $\gamma_i^{(i)}$ does not include the term $\gamma_i{}^\circ$ like eq. (3-10),

$$\ln \frac{\gamma_i(n_1{}^\circ, \cdots, n_{i-1}^\circ, n_i, n_{i+1}^\circ, \cdots, n_{j-1}^\circ, n_j, n_{j+1}^\circ, \cdots, n_k{}^\circ)}{\gamma_i(n_1{}^\circ, \cdots, n_{i-1}^\circ, n_i, n_{i+1}^\circ, \cdots, n_{j-1}^\circ, n_j{}^\circ, n_{j+1}^\circ, \cdots, n_k{}^\circ)}$$
$$= (n_j - n_j{}^\circ)\left[\frac{\partial \ln \gamma_i(n_1{}^\circ, n_2{}^\circ, \cdots, n_k{}^\circ)}{\partial n_j}\right]_{n_l \,;\, l \neq j} \tag{3-2-}$$

$$\gamma_i^{(j)} = \frac{\gamma_i(n_1{}^\circ, \cdots, n_{i-1}^\circ, n_i, n_{i+1}^\circ, \cdots, n_{j-1}^\circ, n_j, n_{j+1}^\circ, \cdots, n_k{}^\circ)}{\gamma_i(n_1{}^\circ, \cdots, n_{i-1}^\circ, n_i, n_{i+1}^\circ, \cdots, n_{j-1}^\circ, n_j{}^\circ, n_{j+1}^\circ, \cdots, n_k{}^\circ)} \tag{3-21}$$

Using the interaction parameter at constant mole fraction ratio defined by eq. (2-64),

$$\left[\frac{\partial \ln \gamma_i(n_1{}^\circ, n_2{}^\circ, \cdots, n_k{}^\circ)}{\partial n_j}\right]_{n_l ; l \neq j} = \beta_i^{(j)} \frac{1-N_j{}^\circ}{\sum\limits_{l=1}^{k} n_l{}^\circ} \tag{3-22}$$

has been derived.[3] Therefore, from eqs. (3-20), (3-21) and (3-22)

$$\ln \gamma_i^{(j)} = \beta_i^{(j)}(N_j-N_j{}^\circ)(1-N_j{}^\circ), \qquad j \neq i, \tag{3-23}$$

is derived, while $\ln \gamma_i^{(i)}$ is expressed as follows:

$$\ln \gamma_i^{(i)} = \ln \gamma_i{}^\circ + \beta_i^{(i)}(N_i-N_i{}^\circ)(1-N_i{}^\circ). \tag{3-24}$$

Thus the following relation is obtained:

$$\ln \gamma_i = \ln \gamma_i{}^\circ + \sum_{j=1}^{k} \beta_i^{(j)}(N_j-N_j{}^\circ)(1-N_j{}^\circ). \tag{3-25}$$

In a similar manner, the relationship between $b_i^{(j)}$ and interaction coefficient $f_i^{(j)}$ is derived as follows:

$$\log f_i^{(j)} = b_i^{(j)}(X_j-X_j{}^\circ)\left(1-\frac{X_j{}^\circ}{100}\right), \qquad j \neq i, \tag{3-26}$$

while

$$\log f_i^{(i)} = \log f_i{}^\circ + b_i^{(i)}(X_i-X_i{}^\circ)\left(1-\frac{X_i{}^\circ}{100}\right). \tag{3-27}$$

Thus the following relation between activity coefficient and the interaction parameter at constant weight percent ratio is obtained:

$$\log f_i = \log f_i{}^\circ + \sum_{j=1}^{k} b_i^{(j)}(X_j-X_j{}^\circ)\left(1-\frac{X_j{}^\circ}{100}\right) \tag{3-28}$$

Eq. (3-26) will be discussed in later section.

In addition, the following equation can be derived from eqs. (2-8) and (3-25),

$$\ln \lambda_i = \ln \frac{\gamma_i{}^\circ}{\gamma_i{}'} + \sum_{j=1}^{k} \beta_i^{(j)}(N_j-N_j{}^\circ)(1-N_j{}^\circ). \tag{3-39}$$

4. Relationship between Various Interaction Parameters at Any Given Concentration

4.1. General relation between interaction parameter at constant mole fraction

The total differential of μ_i is derived from eq. (2-5) as

$$d\mu_i = RT\left[d \ln \gamma_i + \frac{1}{N_i} dN_i\right], \qquad i = 1, 2, \cdots, k \tag{4-1}$$

under the condition of constant temperature and pressure.

Since γ_i is a function of N_2, N_3, $\cdots$, N_k, regarding the first component 1 as solvent, this differential yields

$$\left(\frac{\partial \mu_i}{\partial N_i}\right)_{N_l\,;\,l\neq1,\,i} = RT\left[\left(\frac{\partial \ln \gamma_i}{\partial N_i}\right)_{N_l\,;\,l\neq1,\,i} + \frac{1}{N_i}\right], \qquad i\neq1 \tag{4-2}$$

and

$$\left(\frac{\partial \mu_i}{\partial N_s}\right)_{N_l\,;\,l\neq1,\,s} = RT\left(\frac{\partial \ln \gamma_i}{\partial N_s}\right)_{N_l\,;\,l\neq1,\,s}, \qquad s\neq1,\,i\,. \tag{4-3}$$

The chemical potential μ_i is also expressed as a function of N_2, N_3, $\cdots$, N_k, and, therefore, the following equation is obtained:

$$d\mu_i = \sum_{s=2}^{k}\left(\frac{\partial \mu_i}{\partial N_s}\right)_{N_l\,;\,l\neq1,\,s} dN_s, \qquad s\neq1. \tag{4-4}$$

This equation gives

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{n_l\,;\,l\neq j} = \sum_{s=2}^{k}\left(\frac{\partial \mu_i}{\partial N_s}\right)_{N_l\,;\,l\neq1,\,s}\left(\frac{\partial N_s}{\partial n_j}\right)_{n_l\,;\,l\neq j}, \qquad j=1,2,\cdots,k\,. \tag{4-5}$$

Therefore, substitution of eqs. (2-11), (2-12), (4-2) and (4-3) in eq. (4-5) yields

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{n_l\,;\,l\neq j} = \frac{RT}{\sum_{l=1}^{k} n_l}\left[\left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{N_l\,;\,l\neq1,\,j} - 1\right.$$
$$\left. - \sum_{s=2}^{k}\left(\frac{\partial \ln \gamma_i}{\partial N_s}\right)_{N_l\,;\,l\neq1,\,s} N_s\right], \qquad j\neq1. \tag{4-6}$$

This equation may be rewritten as

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{n_l\,;\,l\neq i} = \frac{RT}{\sum_{l=1}^{k} n_l}\left[\left(\frac{\partial \ln \gamma_j}{\partial N_i}\right)_{N_l\,;\,l\neq1,\,i} - 1\right.$$
$$\left. - \sum_{s=2}^{k}\left(\frac{\partial \ln \gamma_j}{\partial N_s}\right)_{N_l\,;\,l\neq1,\,s} N_s\right], \qquad i\neq1. \tag{4-7}$$

Let G be the Gibbs' free energy of this system, then the following relation is valid at an equilibrium state:

$$dG = \sum_{l=1}^{k} \mu_l dN_l = 0\,. \tag{4-8}$$

Since the function G is continuous with respect to the number of moles, the sequence of differentiation of G with respect to n_j and n_i is immaterial, i.e.

$$\frac{\partial^2 G}{\partial n_i \partial n_j} = \frac{\partial^2 G}{\partial n_j \partial n_i} = \frac{\partial \mu_i}{\partial n_j} = \frac{\partial \mu_j}{\partial n_i} \tag{4-9}$$

which are usually called Maxwell cross differentials. Let us rewrite this, imposing clearly the condition of partial differentiation;

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{n_l \,;\, l \neq j} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{n_l \,;\, l \neq i} \tag{4-10}$$

Introduction of the relation of eq. (4-10) into eqs. (4-6) and (4-7) gives

$$\left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{N_l \,;\, l \neq 1, j} - \sum_{s=2}^{k}\left(\frac{\partial \ln \gamma_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s} N_s$$
$$= \left(\frac{\partial \ln \gamma_j}{\partial N_i}\right)_{N_l \,;\, l \neq 1, i} - \sum_{s=2}^{k}\left(\frac{\partial \ln \gamma_j}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s} N_s, \qquad i, j \neq 1. \tag{4-11}$$

Now, Gibbs-Duhem's equation is given as

$$\sum_{s=1}^{k} n_s d\mu_s = 0, \tag{4-12}$$

and dividing by the total number of moles, one obtains

$$\sum_{s=1}^{k} N_s d\mu_s = 0. \tag{4-13}$$

Therefore, partial differentiation with respect to N_p gives

$$\sum_{s=1}^{k} N_s \left(\frac{\partial \mu_s}{\partial N_p}\right)_{N_l \,;\, l \neq 1, p} = 0, \qquad p \neq 1. \tag{4-14}$$

While, from eq. (4-1)

$$\left(\frac{\partial \mu_1}{\partial N_p}\right)_{N_l \,;\, l \neq 1, p} = RT\left[\left(\frac{\partial \ln \gamma_1}{\partial N_p}\right)_{N_l \,;\, l \neq 1, p} - \frac{1}{N_1}\right]. \tag{4-15}$$

It is thus readily shown that eq. (4-14) results:

$$\sum_{s=1}^{k} \left(\frac{\partial \ln \gamma_s}{\partial N_p}\right)_{N_l \,;\, l \neq 1, p} N_s = 0, \qquad p \neq 1. \tag{4-16}$$

This equation can be generalized as

$$\sum_{s=1}^{k} \left(\frac{\partial \ln \gamma_s}{\partial N_p}\right)_{N_l \,;\, l \neq p, q} N_s = 0, \qquad p \neq q \tag{4-17}$$

Since $\ln \gamma_i$ is considered as a function of $N_2, N_3, \cdots, N_k$, the total differential can be shown:

$$d\ln \gamma_i = \sum_{s=2}^{k} \left(\frac{\partial \ln \gamma_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1, s} dN_s. \tag{4-18}$$

Consequently, if only N_p and N_q are variable and the other mole fractions are constant, the interaction parameter under this condition may be calculated from the above equation:

$$\left(\frac{\partial \ln \gamma_i}{\partial N_p}\right)_{N_l \,;\, l \neq p, q} = \left(\frac{\partial \ln \gamma_i}{\partial N_p}\right)_{N_l \,;\, l \neq 1, p} - \left(\frac{\partial \ln \gamma_i}{\partial N_q}\right)_{N_l \,;\, l \neq 1, q}. \tag{4-19}$$

Furthermore, it is clear that the following general relation holds:

$$\left(\frac{\partial \ln \gamma_i}{\partial N_p}\right)_{N_l\,;\,l\,\neq\,p,\,q} = -\left(\frac{\partial \ln \gamma_i}{\partial N_q}\right)_{N_l\,;\,l\,\neq\,p,\,q}. \qquad (4\text{-}20)$$

Among the preceding relationship, eqs. (4-11), (4-16), (4-19) and (4-20) are especially important in order to calculate the relation between the interaction parameters at constant mole fractions.

On the other hand, since $\gamma_i{}'$ in eq. (2-25) is a constant value at the fixed point of $N_i=0$, $N_l=N_l{}^\circ$; $l \neq i$, this equation yields

$$d\mu_i = RT\left[d\ln\lambda_i + \frac{1}{N_i}dN_i\right], \qquad (4\text{-}21)$$

and λ_i is also a function of mole fractions, therefore, the relationship between interaction parameters at constant mole fractions on Henrian basis can be shown quite as the same type equations only by substitution of λ_i instead of γ_i. This means that the value of interaction parameters at constant mole fractions is independent of the selection of reference states.

4.2. General relations between interaction parameters at constant weight percents

The relationship between these interaction parameters can be derived by using eq. (2-54) or (2-55).

Since, from eq. (2-54) or (2-55), the total differential of μ_i is given by

$$d\mu_i = RT\left[d\ln f_i + \frac{1}{X_i}dX_i\right], \qquad (4\text{-}22)$$

consequently, one obtains by partial differentiation:

$$\left(\frac{\partial \mu_i}{\partial X_i}\right)_{X_l\,;\,\neq 1,\,i} = RT\left[\left(\frac{\partial \ln f_i}{\partial X_i}\right)_{X_l\,;\,l\,\neq 1,\,i} + \frac{1}{X_i}\right], \quad i \neq 1, \qquad (4\text{-}23)$$

$$\left(\frac{\partial \mu_i}{\partial X_s}\right)_{X_l\,;\,l\,\neq 1,\,s} = RT\left(\frac{\partial \ln f_i}{\partial X_s}\right)_{X_l\,;\,l\,\neq 1,\,s}, \quad s \neq i, 1 \qquad (4\text{-}24)$$

Then the expansion of μ_i with respect to the weight percents of each component is

$$d\mu_i = \sum_{s=2}^{k}\left(\frac{\partial \mu_i}{\partial X_s}\right)_{X_l\,;\,l\,\neq 1,\,s}dX_s, \qquad (4\text{-}25)$$

thus we obtain

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{n_l\,;\,l\,\neq j} = \sum_{s=2}^{k}\left(\frac{\partial \mu_i}{\partial X_s}\right)_{X_l\,;\,l\,\neq 1,\,s}\left(\frac{\partial X_s}{\partial n_j}\right)_{n_l\,;\,l\,\neq j}, \quad j=1,2,\cdots,k. \qquad (4\text{-}26)$$

Substitution of eqs. (4-23), (4-24), (2-44) and (2-45) in this equation gives the following relation:

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{n_l:l\neq j} = -\frac{M_j RT}{\sum\limits_{l=1}^{k} M_l n_l}\left[100\left(\frac{\partial \ln f_i}{\partial X_j}\right)_{X_l:l\neq 1,j} - 1\right.$$

$$\left. - \sum_{s=2}^{k}\left(\frac{\partial \ln f_i}{\partial X_s}\right)_{X_l:l\neq 1,s} X_s\right], \qquad j\neq 1 \qquad (4\text{-}27)$$

Next equation is thus derived by Maxwell cross differentials:

$$M_j\left[100\left(\frac{\partial \log f_i}{\partial X_j}\right)_{V_l:l\neq 1,j} - \sum_{s=2}^{k}\left(\frac{\partial \log f_i}{\partial X_s}\right)_{X_l:l\neq 1,s} - \frac{1}{2.303}\right]$$

$$= M_i\left[100\left(\frac{\partial \log f_j}{\partial X_i}\right)_{X_l:l\neq 1,i} - \sum_{s=2}^{k}\left(\frac{\partial \log f_j}{\partial X_s}\right)_{X_l:l\neq 1,s} - \frac{1}{2.303}\right], \quad i,j\neq 1. \quad (4\text{-}28)$$

From Gibbs-Duhem equation, by substituting eq. (2-32) in (4-13) and then dividing it with dX_p

$$\sum_{s=1}^{k} \frac{X_s}{M_s}\left(\frac{\partial \mu_s}{\partial X_p}\right)_{X:l\neq 1,p} = 0, \qquad (4\text{-}29)$$

and from eq. (4-22)

$$\left(\frac{\partial \mu_1}{\partial X_p}\right)_{X_l:l\neq 1,p} = RT\left[\left(\frac{\partial \ln f_1}{\partial X_p}\right)_{X_l:l\neq 1,p} - \frac{1}{X_1}\right] \qquad (4\text{-}30)$$

are obtained.   Hence, substitution of eqs. (4-30), (2-33) and (2-45) in eq. (4-29) yields

$$2.303\sum_{s=1}^{k} \frac{X_s}{M_s}\left(\frac{\partial \log f_s}{\partial X_p}\right)_{X_l:l\neq 1,p} + \frac{1}{M_p} - \frac{1}{M_1} = 0, \qquad p\neq 1 \qquad (4\text{-}31)$$

General form of this equation is

$$2.303\sum_{s=1}^{k} \frac{X_s}{M_s}\left(\frac{\partial \log f_s}{\partial X_p}\right)_{X_l:l\neq p,q} + \frac{1}{M_p} - \frac{1}{M_q} = 0, \qquad p\neq q. \qquad (4\text{-}32)$$

Since f_i is a function of weight percents, the total differential of $\log f_i$ is given by

$$d\log f_i = \sum_{s=2}^{k}\left(\frac{\partial \log f_i}{\partial X_s}\right)_{X_l:l\neq 1,s} dX_s. \qquad (4\text{-}33)$$

From the above equation, the following relations are derived in a similar manner as in preceding section:

$$\left(\frac{\partial \log f_i}{\partial X_p}\right)_{X_l:l\neq p,q} = \left(\frac{\partial \log f_i}{\partial X_p}\right)_{X_l:l\neq 1,p} - \left(\frac{\partial \log f_i}{\partial X_q}\right)_{X_l:l\neq 1,q}, \quad p,q\neq 1,\ p\neq q \qquad (4\text{-}34)$$

and

$$\left(\frac{\partial \log f_i}{\partial X_p}\right)_{X_l:l\neq p,q} = -\left(\frac{\partial \log f_i}{\partial X_q}\right)_{X_l:l\neq p,q}, \qquad p\neq q. \qquad (4\text{-}35)$$

4. 3. General relations between interaction parameters at constant weight percent ratio

The relation between the interaction parameters defined by

$$b_i^{(j)} = \left(\frac{\partial \log f_i}{\partial X_j}\right)_{X_1/X_2/\cdots/X_{j-1}/X_{j+1}/\cdots/X_k} \tag{2-65}$$

has never been given, and so let us derive the relation.

Now, if only n_j is variable and the other number of moles are constant, the following relation is obtained from eq. (2-44):

$$\left(\frac{\partial X_p}{\partial X_q}\right)_{n_l\,;\,l\neq j} = \left(\frac{\partial X_p}{\partial n_j}\right)_{n_l\,;\,l\neq j} \Big/ \left(\frac{\partial X_q}{\partial n_j}\right)_{n_l\,;\,l\neq j}$$

$$= \frac{X_p}{X_q} = \frac{M_p n_p}{M_q n_q}. \tag{4-36}$$

Since atomic weight M_p and M_q are constant, each term of eq. (4-36) is constant for the case of constant n_p and n_q. Therefore, partial differentiation of some function with respect to n_j under the condition of constant number of moles except n_j corresponds to partial differentiation with respect to X_j under that of constant weight percent ratio except X_j. These relationship will be explained in Appendix B for the case of ternary system.

From eq. (4-22),

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{n_l\,;\,l\neq j} = RT\left[\left(\frac{\partial \ln f_i}{\partial n_j}\right)_{n_l\,;\,l\neq j} + \frac{1}{X_i}\left(\frac{\partial X_i}{\partial n_j}\right)_{n_l\,;\,l\neq j}\right] \tag{4-37}$$

and, as mentioned above, the first term in bracket of the right-hand side of this equation may be rewritten as

$$\left(\frac{\partial \ln f_i}{\partial n_j}\right)_{n_l\,;\,l\neq j} = \left(\frac{\partial \ln f_i}{\partial X_j}\right)_{X_1/X_2/\cdots/X_{j-1}/X_{j+1}/\cdots/X_k}\left(\frac{\partial X_j}{\partial n_j}\right)_{n_l\,;\,l\neq j}. \tag{4-38}$$

Upon substitution of eq. (2-65) in eq. (4-38), it follows that

$$\left(\frac{\partial \ln f_i}{\partial n_j}\right)_{n_l\,;\,l\neq j} = 2.303\, b_i^{(j)}\left(\frac{\partial X_j}{\partial n_j}\right)_{n_l\,;\,l\neq j}. \tag{4-39}$$

Introducting eq. (4-39) and the relations of eqs. (2-44) and (2-45) into eq. (4-37), the following equation is obtained:

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{n_l\,;\,l\neq j} = \frac{M_j RT}{\sum\limits_{l=1}^{k} M_l n_l}[2.303\, b_j^{(i)}(100-X_j)-1]. \tag{4-40}$$

By the aid of Maxwell cross differential relation, it follows that

$$M_j[2.303\, b_i^{(j)}(100-X_j)-1] = M_i[2.303\, b_j^{(i)}(100-X_i)-1]. \tag{4-41}$$

Gibbs-Duhem enuation may be converted as follows by substitution of eq. (2-32) in eq. (4-13) and dividing with dn_p:

$$\sum_{s=1}^{k} \frac{X_s}{M_s} \left(\frac{\partial \mu_s}{\partial n_p} \right)_{n_l \,;\, l \neq p} = 0, \tag{4-42}$$

and so, considering the relations (4-39), (2-44) and (2-45), this yields

$$\sum_{s=1}^{k} \frac{X_s}{M_s} [2.303\, b_s^{(p)}(100-X_p)-1] + \frac{100}{M_p} = 0. \tag{4-43}$$

Furthermore, using eq. (4-41), the following equation can be derived:

$$\sum_{s=1}^{k} X_s b_p^{(s)}(100-X_s) = 0. \tag{4-44}$$

5. The Relationship between Several Kinds of Interaction Parameters

5.1. Relation between interaction parameters at constant mole fractions and those at constant weight percent

Eq. (2-40) may be rewritten by introduction of eqs. (2-1) and (2-39):

$$f_i X_i = \gamma_i N_i \frac{M_i}{\gamma_i'} \sum_{\substack{l=1 \\ l \neq i}}^{k} \frac{X_l{}^\circ}{M_l}. \tag{5-1}$$

Since γ_i', M_l and $X_l{}^\circ$ are constant, the total differential of the logarithm of both sides of this equation is

$$d \ln f_i + d \ln X_i = d \ln \gamma_i + d \ln N_i. \tag{5-2}$$

Dividing this equation with respect to dN_j, one obtains

$$\left(\frac{\partial \ln \gamma_i}{\partial N_j} \right)_{N_l \,;\, l \neq 1,\, j} = \left(\frac{\partial \ln f_i}{\partial N_j} \right)_{N_l \,;\, l \neq 1,\, j} + \frac{1}{X_i} \left(\frac{\partial X_i}{\partial N_j} \right)_{N_l \,;\, l \neq 1,\, j} \tag{5-3}$$

While from the relation

$$d \ln f_i = \sum_{s=2}^{k} \left(\frac{\partial \ln f_i}{\partial X_s} \right)_{X_l \,;\, l \neq 1,\, s} dX_s, \tag{5-4}$$

we obtain the following equation:

$$\left(\frac{\partial \ln f_i}{\partial N_j} \right)_{N_l \,;\, \neq 1,\, j} = \sum_{s=2}^{k} \left(\frac{\partial \ln f_i}{\partial X_s} \right)_{X_l \,;\, \neq 1,\, s} \left(\frac{\partial X_s}{\partial N_j} \right)_{N_l \,;\, l \neq 1,\, j}. \tag{5-5}$$

The relation between weight percent and mole fractions is given by

$$X_s = \frac{100\, M_s N_s}{M_1 + \sum_{l=1}^{k} (M_l - M_1) N_l}, \tag{5-6}$$

then the following equations are derived;

$$\left(\frac{\partial X_s}{\partial N_j}\right)_{N_l \,;\, l \neq 1,\, j} = -X_s \frac{M_j - M_1}{\sum\limits_{l=1}^{k} M_l N_l}, \qquad s \neq j \tag{5-7}$$

$$\left(\frac{\partial X_j}{\partial N_j}\right)_{N_l \,;\, \neq 1,\, j} = -X_j \frac{M_j - M_1}{\sum\limits_{l=1}^{k} M_l N_l} + \frac{100\, M_j}{\sum\limits_{l=1}^{k} M_l N_l}. \tag{5-8}$$

From the general relation:

$$X_s = M_s N_s \sum_{l=1}^{k} \frac{X_l}{M_l}, \tag{5-9}$$

$$\frac{1}{\sum\limits_{l=1}^{k} M_l N_l} = \frac{1}{100} \sum_{l=1}^{k} \frac{X_l}{M_l}. \tag{5-10}$$

Substitution of eqs. (5-5), (5-7), (5-8) and (5-10) in eq. (5-3) yields

$$\left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{N_l \,;\, \neq 1,\, j} = \frac{2.303}{100} \sum_{l=1}^{k} \frac{X_l}{M_l} \left[100\, M_j \left(\frac{\partial \log f_i}{\partial X_j}\right)_{X_l \,;\, l \neq 1,\, j} - \frac{M_j - M_1}{2.303} \right.$$
$$\left. - (M_j - M_1) \sum_{s=2}^{k} \left(\frac{\partial \log f_i}{\partial X_s}\right)_{X_l \,;\, l \neq 1,\, s} X_s \right]. \tag{5-11}$$

Calculation from the following equation which is derived from eq. (5-2) instead of eq. (5-3):

$$\left(\frac{\partial \ln f_i}{\partial X_j}\right)_{X_l \,;\, l \neq 1,\, j} = \left(\frac{\partial \ln \gamma_i}{\partial X_j}\right)_{X_l \,;\, l \neq 1,\, j} + \frac{1}{N_i} \left(\frac{\partial N_i}{\partial X_j}\right)_{X_l \,;\, l \neq 1,\, j} \tag{5-12}$$

gives the following relation:

$$\left(\frac{\partial \log f_i}{\partial X_j}\right)_{X_l \,;\, l \neq 1,\, j} = \frac{\sum\limits_{l=1}^{k} M_l N_l}{230.3} \left[\frac{1}{M_j} \left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{N_l \,;\, l \neq 1,\, j} - \left(\frac{1}{M_j} - \frac{1}{M_1}\right) \right.$$
$$\left. - \left(\frac{1}{M_j} - \frac{1}{M_1}\right) \sum_{s=2}^{k} \left(\frac{\partial \ln \gamma_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1,\, s} N_s \right]. \tag{5-13}$$

Furthermore, using the following relation:

$$\sum_{l=1}^{k} n_l \sum_{l=1}^{k} M_l N_l = \sum_{l=1}^{k} M_l n_l \tag{5-14}$$

and upon combination of eqs. (4-6) and (4-27) together with eq. (5-10), it follows that

$$\left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{N_l \,;\, \neq 1,\, j} - \sum_{s=2}^{k} \left(\frac{\partial \ln \gamma_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1,\, s} N_s - 1$$
$$= \frac{2.303}{100} M_i \sum_{l=1}^{k} \frac{X_l}{M_l} \left[100 \left(\frac{\partial \log f_i}{\partial X_j}\right)_{X_l \,;\, l \neq 1,\, j} - \sum_{s=2}^{k} \left(\frac{\partial \log f_i}{\partial X_s}\right)_{X_l \,;\, l \neq 1,\, s} X_s - \frac{1}{2.303} \right]. \tag{5-15}$$

Equation (5-11), (5-13) and (5-15) can be converted to each other,

5.2. Relation between interaction parameter at constant mole fraction ratio and that at constant weight percent ratio

Iateraction parameter at constant mole fraction ratio is related to the chemical potential as follows[3]

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{n_l \,;\, l \neq j} = \frac{RT}{\sum\limits_{l=1}^{k} n_l}[\beta_i^{(j)}(1-N_j)-1].$$ (5-16)

The left-hand side of this equation is identical with that of eq. (4-40), therefore using eq. (5-14), we obtain the following relation between $\beta_i^{(j)}$ and $b_i^{(j)}$:

$$\beta_i^{(j)}(1-N_j)-1 = \frac{M_j}{\sum\limits_{l=1}^{k} M_l N_l}[2.303\, b_i^{(j)}(100-X_j)-1].$$ (5-17)

Moreover, relation (5-10) makes this equation to the following form:

$$\beta_i^{(j)} = \frac{M_i\left(\sum\limits_{l=1}^{k}\frac{X_l}{M_l}\right)^2[2.303\, b_i^{(j)}(100-X_j)-1]+100\sum\limits_{l=1}^{k}\frac{X_l}{M_l}}{100\left(\sum\limits_{l=1}^{k}\frac{X_l}{M_l}-\frac{X_j}{M_j}\right)}.$$ (5-18)

Indeed, the calculation using

$$\left(\frac{\partial \ln f_i}{\partial n_j}\right)_{n_l \,;\, l \neq j}+\frac{1}{X_i}\left(\frac{\partial X_i}{\partial n_j}\right)_{n_l \,;\, l \neq j} = \left(\frac{\partial \ln \gamma_i}{\partial n_j}\right)_{n_l \,;\, l \neq j}+\frac{1}{N_i}\left(\frac{\partial N_i}{\partial n_j}\right)_{n_l \,;\, l \neq j}$$ (5-19)

which is derived from eq. (5-2), also results the same relation.

5.3. Relation between interaction parameters at constant mole fraction and at constant activity, and solubility parameter

When the activity of component i is constant, eq. (4-1) yields

$$d\mu_i = RT\left(d\ln \gamma_i+\frac{1}{N_i}dN_i\right) = 0.$$ (5-20)

Hence, substituting eq. (4-18) in eq. (5-20) and in view of eq. (1-68), it follows that

$$\sum\limits_{s=2}^{k}\left(\frac{\partial \ln \gamma_i}{\partial N_s}\right)_{N_l \,;\, l \neq 1,s}\frac{1}{m_i^{(s)}}+\frac{1}{N_i} = 0,$$ (5-21)

and in the case of solubility parameter concerning component itself,

$$m_i^{(i)} = 1.$$ (5-22)

Now, one obtains from eq. (5-20).

$$\epsilon_i^{(j)}a = \left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{a_i} = -\left(\frac{\partial \ln N_i}{\partial N_j}\right)_{a_i} = -\frac{1}{N_i}\left(\frac{\partial N_i}{\partial N_j}\right)_{a_i} = -\frac{m_i^{(j)}}{N_i},$$ (5-23)

then, eq. (5–21) becomes

$$\sum_{s=2}^{k} \left(\frac{\partial \ln \gamma_i}{\partial N_s} \right)_{N_l\,;\,l\neq 1, s} \frac{1}{\varepsilon_i^{(s)} a} = 1 \,, \tag{5-24}$$

where

$$\varepsilon_i^{(t)} a = -\frac{1}{N_i} \,. \tag{5-25}$$

5.4. Relation between interaction parameters at constant weight percent and at constant activity parameter

When $a_i(\%)$ is constant, one obtains from eq. (2–39)

$$d \ln f_i = -d \ln X_i = -\frac{1}{X_i} dX_i \,. \tag{5-26}$$

Consequently

$$\left(\frac{\partial \ln f_i}{\partial X_j} \right)_{a_i} = -\frac{1}{X_i} \left(\frac{\partial X_i}{\partial X_j} \right)_{a_i} \tag{5-27}$$

i.e.

$$e_i^{(j)} a = -\frac{m_i'^{(j)}}{2.303 X_i} \tag{5-28}$$

which has been derived by H. Schenck et al.[7]

On the other hand, using eq. (4–33),

$$\sum_{s=2}^{k} \left(\frac{\partial \log f_i}{\partial X_s} \right)_{X_l\,;\,l\neq 1, s} \frac{1}{m_i'^{(s)}} = -\frac{1}{2.303 X_i} \,, \tag{5-29}$$

and substitution of eq. (5–28) gives

$$\sum_{s=2}^{k} \left(\frac{\partial \log f_i}{\partial X_s} \right)_{X_l\,;\,l\neq 1, s} \frac{1}{e_i^{(s)} a} = 1 \,, \tag{5-30}$$

where it is apparent from the definition that the followings are substantiated:

$$m_i'^{(t)} = 1 \,, \tag{5-31}$$

$$e_i^{(t)} a = -\frac{1}{2.303 X_i} \,. \tag{5-32}$$

5.5. Relation between interaction parameters at constant mole fractions and at constant mole fraction ratio

Since the interaction parameter at constant mole fraction ratio is related to the chemical potential as eq. (5–16), identifying this and eq. (4–6), we can obtain the following relation:

$$\beta_i^{(j)}(1 - N_j) = \left(\frac{\partial \ln \gamma_i}{\partial N_j} \right)_{N_l\,;\,l\neq 1, j} - \sum_{s=2}^{k} \left(\frac{\partial \log \gamma_i}{\partial N_s} \right)_{N_l\,;\,l\neq 1, s} N_s, \quad j \neq 1 \,. \tag{5-33}$$

When $j=1$ in eq. (4–5), the following equations are obtained:

$$\left(\frac{\partial \mu_i}{\partial n_1}\right)_{n_l\,;\,l\neq 1} = \sum_{s=2}^{k} \left(\frac{\partial \mu_i}{\partial N_s}\right)_{N_l\,;\,l\neq 1,s} \left(\frac{\partial N_s}{\partial n_1}\right)_{n_l\,;\,l\neq 1} \tag{5-34}$$

$$\therefore \quad \left(\frac{\partial \mu_i}{\partial n_1}\right)_{n_l\,;\,l\neq 1} = \frac{RT}{\sum\limits_{l=0}^{k} n_l} \left[\sum_{s=2}^{k} \left(\frac{\partial \ln \gamma_i}{\partial N_s}\right)_{N_l\,;\,l\neq 1,s} N_s + 1\right]. \tag{5-35}$$

Upon combining eq. (5-16) with eq. (5-35) for the case of $j=1$, it follows that

$$\beta_i^{(1)}(1-N_1) = -\sum_{s=2}^{k} \left(\frac{\partial \ln \gamma_i}{\partial N_s}\right)_{N_l\,;\,l\neq 1,s} N_s, \tag{5-36}$$

Therefore we obtain the following relation[3] by substracting eq. (5-36) from eq. (5-33):

$$\left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{N_l\,;\,l\neq 1,j} = \beta_i^{(j)}(1-N_j) - \beta_i^{(1)}(1-N_1). \tag{5-37}$$

This relation can be derived also from eq. (3-23) in section 3 (see Appendix C).

5.6. Relation between interaction parameter at constant weight parcents and at constant weight percent ratio

Combination of eqs. (4-27) and (4-40) gives the conversion equation between interaction parameter at constant weight percents and that at constant weight percent ratio:

$$b_i^{(j)}(100-X_j) = 100\left(\frac{\partial \log f_i}{\partial X_j}\right)_{X_l\,;\,l\neq 1,j} - \sum_{s=2}^{k} \left(\frac{\partial \log f_i}{\partial X_s}\right)_{X_l\,;\,l\neq 1,s} X_s, \quad j\neq 1 \tag{5-38}$$

If the condition $j=1$ is given to eq. (4-26), it follows that

$$\left(\frac{\partial \mu_i}{\partial n_1}\right)_{n_l\,;\,l\neq 1} = \sum_{s=2}^{k} \left(\frac{\partial \mu_i}{\partial X_s}\right)_{X_l\,;\,l\neq 1,s} \left(\frac{\partial X_s}{\partial n_1}\right)_{n_l\,;\,l\neq 1}, \tag{5-39}$$

and using the relations (4-23), (4-24) and (2-44), the above equation yields

$$\left(\frac{\partial \mu_i}{\partial n_1}\right)_{n_l\,;\,l\neq 1} = -\frac{M_1 RT}{\sum\limits_{l=1}^{k} M_l n_l} \left[\sum_{s=2}^{k} \left(\frac{\partial \log f_i}{\partial X_s}\right)_{X_l\,;\,l\neq 1,s} X_s + 1\right]. \tag{5-40}$$

This equation is identical with eq. (4-40) at the condition $j=1$, and therefore,

$$b_i^{(1)}(100-X_1) = -\sum_{s=2}^{k} \left(\frac{\partial \log f_i}{\partial X_s}\right)_{X_l\,;\,l\neq 1,s} X_s. \tag{5-51}$$

Substraction of eq. (5-41) from (5-38) gives

$$\left(\frac{\partial \log f_i}{\partial X_j}\right)_{X_l\,;\,l\neq 1,j} = b_i^{(j)}\left(1-\frac{X_j}{100}\right) - b_i^{(j)}\left(1-\frac{X_1}{100}\right) \tag{5-42}$$

This relation can, like the case of eq. (5-37), be derived also from eq. (3-25), by using the same method as described in Appendix C.

6. Application to Ternary System

In the preceding sections, general relationship between various interaction parameters in multicomponent solution has been discussed. Now, in this section, the applications in ternary system are treated. In ternary solution, we can obtain some comparatively simple relations.

In the first place, we may put $k=3$ in eq. (4-11), because we are considering ternary system, and when $i=2$, $j=3$, we obtain

$$\left(\frac{\partial \ln \gamma_2}{\partial N_2}\right)_{N_3} N_2 - \left(\frac{\partial \ln \gamma_2}{\partial N_3}\right)_{N_2} (1-N_3) = \left(\frac{\partial \ln \gamma_3}{\partial N_3}\right)_{N_2} N_3 - \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} (1-N_2). \qquad (6\text{-}1)$$

Eq. (4-16) gives

$$\left(\frac{\partial \ln \gamma_1}{\partial N_2}\right)_{N_3} N_1 + \left(\frac{\partial \ln \gamma_2}{\partial N_2}\right)_{N_3} N_2 + \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} N_3 = 0, \qquad (6\text{-}2)$$

$$\left(\frac{\partial \ln \gamma_1}{\partial N_3}\right)_{N_2} N_1 + \left(\frac{\partial \ln \gamma_2}{\partial N_3}\right)_{N_2} N_2 + \left(\frac{\partial \ln \gamma_3}{\partial N_3}\right)_{N_2} N_3 = 0. \qquad (6\text{-}3)$$

Subtracting eq. (6-3) from eq. (6-2), and substituting the following relation obtained from eq. (4-19):

$$\left(\frac{\partial \ln \gamma_1}{\partial N_2}\right)_{N_1} = \left(\frac{\partial \ln \gamma_1}{\partial N_2}\right)_{N_2} - \left(\frac{\partial \ln \gamma_1}{\partial N_3}\right)_{N_2}, \qquad (6\text{-}4)$$

then

$$\left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} = \left(\frac{\partial \ln \gamma_2}{\partial N_s}\right)_{N_2} + \left(\frac{\partial \ln \gamma_1}{\partial N_2}\right)_{N_1}. \qquad (6\text{-}5)$$

is derived. This is one of the most important relations among tne interaction parameters at constant mole fractions.

In a similar manner, upon putting $k=3$, $i=2$, $j=3$ in eq. (4-28), it follows that

$$\frac{100-X_3}{M_2}\left(\frac{\partial \log f_2}{\partial X_3}\right)_{X_2} - \frac{X_2}{M_2}\left(\frac{\partial \log f_2}{\partial X_2}\right)_{X_3} - \frac{1}{2.303 M_2}$$
$$= \frac{100-X_2}{M_3}\left(\frac{\partial \log f_3}{\partial X_2}\right)_{X_3} - \frac{X_3}{M_3}\left(\frac{\partial \log f_3}{\partial X_3}\right)_{X_2} - \frac{1}{2.303 M_3}, \qquad (6\text{-}6)$$

and eq. (4-31) gives

$$\frac{X_1}{M_1}\left(\frac{\partial \log f_1}{\partial X_2}\right)_{X_3} + \frac{X_2}{M_2}\left(\frac{\partial \log f_2}{\partial X_2}\right)_{X_3} + \frac{X_3}{M_3}\left(\frac{\partial \log f_3}{\partial X_2}\right)_{X_3} + \frac{1}{2.303}\left(\frac{1}{M_2}-\frac{1}{M_1}\right) = 0, \qquad ((6\text{-}7)$$

$$\frac{X_1}{M_1}\left(\frac{\partial \log f_1}{\partial X_3}\right)_{X_2} + \frac{X_2}{M_2}\left(\frac{\partial \log f_2}{\partial X_3}\right)_{X_2} + \frac{X_3}{M_3}\left(\frac{\partial \log f_3}{\partial X_3}\right)_{X_2} + \frac{1}{2.303}\left(\frac{1}{M_3}-\frac{1}{M_1}\right) = 0, \qquad (6\text{-}8)$$

while from eq. (4-34) one obtains

$$\left(\frac{\partial \log f_1}{\partial X_2}\right)_{X_1} = \left(\frac{\partial \log f_1}{\partial X_2}\right)_{X_3} - \left(\frac{\partial \log f_1}{\partial X_3}\right)_{X_2}. \tag{6-9}$$

These three equations result the following relation:

$$\frac{1}{M_3}\left(\frac{\partial \log f_3}{\partial X_2}\right)_{X_3} = \frac{1}{M_2}\left(\frac{\partial \log f_2}{\partial X_3}\right)_{X_2} + \frac{1}{M_1}\left(\frac{\partial \log f_1}{\partial X_2}\right)_{X_1}. \tag{6-10}$$

This is also one of the most important relations among the interaction parameters at constant weight percents.

Eqs. (6-5) and (6-10) clearly show that, when the value of interaction parameter representing the effect of addition of the component 2 on activity coefficient of the component 3 is known, for the purpose of calculating the interaction papameter representing the effect of the component 3 on that of the component 2, it is generally necessary concerning a concentrated solution to know the effect of the component 2 or 3 on activity coefficient of the component 1.

However, the conversion between the interaction parameters at constant concentration ratio is easy. Using Maxwell cross differentials, eq. (5-16) yields yields

$$\beta_3^{(2)}(1-N_2) = \beta_2^{(3)}(1-N_3).^{3),7)} \tag{6-11}$$

While, from eq. (4-41) one obtains

$$M_2[2.303b_3^{(2)}(100-X_2)-1] = M_3[2.303b_2^{(3)}(100-X_3)-1]. \tag{6-12}$$

Using either of these equations, $\beta_3^{(2)}$ or $b_3^{(2)}$ is converted straightforward to $\beta_2^{(3)}$ or $b_2^{(3)}$, respectively. Moreover, the conversion from β to b is possible from the relation of eq. (5-18).

The following equations are derived from eq. (5-33)

$$\beta_3^{(2)}(1-N_2) = \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3}(1-N_2) - \left(\frac{\partial \ln \gamma_3}{\partial N_3}\right)_{N_2}N_3, \tag{6-13}$$

$$\beta_3^{(3)}(1-N_3) = \left(\frac{\partial \ln \gamma_3}{\partial N_3}\right)_{N_2}(1-N_3) - \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3}N_2. \tag{6-14}$$

Elimination of $(\partial \ln \gamma_3/\partial N_3)_{N_2}$ from these two equations gives

$$\left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} = \beta_3^{(2)}\frac{(1-N_2)(1-N_3)}{N_1} + \beta_3^{(3)}\frac{(1-N_3)N_3}{N_1}.^{3)} \tag{6-15}$$

in a similar manner, one obtains from eq. (5-38)

$$\left(\frac{\partial \log f_3}{\partial X_2}\right)_{X_3} = b_3^{(2)}\frac{(100-X_2)(100-X_3)}{100X_1} + b_3^{(3)}\frac{(100-X_3)X_3}{100X_1}. \tag{9-16}$$

Eqs. (6-13) to (6-16) have the following geometrical meaning.

Use of a Taylor series expansion of $\ln \gamma_i$ as a linear function of the mole fractions without involving second and higher derivatives corresponds to the substitution of the curved surface of $\ln \gamma_i$ by the tangential plane at a given point of that curved surface, and the interaction parameters correspond to the gradients of the plane determined by each condition of the partial derivatives.

The tangential plane of $\ln \gamma_3$ or $\log f_3$ at any given point in ternary solution represents a normal two dimensional plane, and this plane can generally be determined only when the gradients of two different directions are given. For example, eq. (6-15) is qualitatively explained from the above consideration as follows: When the two interaction parameters $\beta_3^{(2)}$ and $\beta_3^{(3)}$ representing the gradients of $\ln \gamma_3$ on the lines $N_1/N_3 =$ const. and $N_1/N_2 =$ const. respectively are given, the position of the tangential plane of $\ln \gamma_3$ is fixed, then, the gradient of $\ln \gamma_3$ on the line $N_3 =$ const. is consequently determined by this plane. These relation is shown in Fig. 4.
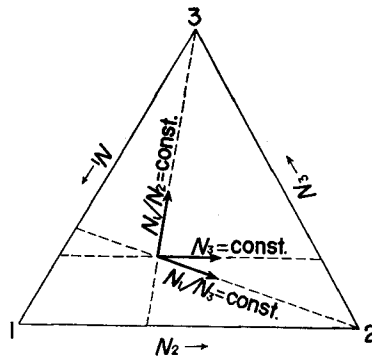

Fig. 4. Relation between interaction parameter at constant mole fraction and that at constant mole fraction ratio.

Conversion equation between solubility parameter $m_3^{(2)}$ and interaction parameter at constant mole fractions is given from eq. (5-21), as

$$m_3^{(2)} = -\frac{\left(\dfrac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_2} N_3}{1 + \left(\dfrac{\partial \ln \gamma_3}{\partial N_3}\right)_{N_2} N_3}, \qquad (6\text{-}17)$$

and likewise conversion equation between interaction parameters at constant activity and at constant mole fractions is derived from eq. (5-24)

$$\varepsilon_3^{(2)} a = \frac{\left(\dfrac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_2}}{1 + \left(\dfrac{\partial \ln \gamma_3}{\partial N_3}\right)_{N_2} N_3}. \qquad (6\text{-}18)$$

The above equation has been derived by T. Fuwa and J. Chipman,[8] and T. Mori, K. Aketa, H. Ono and H. Sugita.[9]

Relation between solubility parameter $m_3'^{(2)}$ and interaction parameter at constant weight percents can be obtained from eq. (5-29):

$$m'^{(2)}_3 = -\frac{2.303\left(\dfrac{\partial \log f_3}{\partial X_2}\right)_{X_3} X_3}{1+2.303\left(\dfrac{\partial \log f_3}{\partial X_3}\right)_{X_2} X_2}, \tag{6-19}$$

and similar relation between interaction parameters at constant activity and at constant weight percents can be obtained from eq. (5-30):

$$e^{(2)}_3 a = \frac{\left(\dfrac{\partial \log f_3}{\partial X_2}\right)_{X_3}}{1+2.303\left(\dfrac{\partial \log f_3}{\partial X_3}\right)_{X_2} X_3} \tag{6-20}$$

Quite the similar consideration as explained above can be applied to eqs. (6-17) to (6-20), that is, when the gradients of $\ln \gamma_3$ on the lines $N_2 = $ const. and $N_3 = $ const. are given, the tangential plane of $\ln \gamma_3$ is fixed, and then the gradient of $\ln \gamma_3$ on $a_3 = $ const. line is determined. (Fig. 5).

Conversion equation between interaction parameters at constant concentrations is given, say from eq. (5-11), by

Fig. 5. Relation between interaction parameter at constant mole fraction and that at constant activity.

$$\left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} = \frac{2.303}{100}\left(\frac{X_1}{M_1}+\frac{X_2}{M_2}+\frac{X_3}{M_3}\right)\left[\left(\frac{\partial \log f_3}{\partial X_2}\right)_{X_3}\{(100-X_2)M_2+M_1 X_2\}\right.$$
$$\left.-(M_2-M_1)\left(\frac{\partial \log f_3}{\partial X_3}\right)_{X_2} X_3-\frac{M_2-M_1}{2.303}\right]. \tag{6-21}$$

We know from the above equations that the experimental determination of only one kind of interaction papameters is insufficient in order to calculate other kinds of them. But, on the contrary, we can calculate the interaction parameter, representing the effect of alloying element on its own activity coefficient, i.e. $(\partial f_3/\partial X_3)_{X_2}$ from eq. (6-21) by arrangement of the same experimented data both on mole fractions and weight percent. We can determine the value of $(\partial \gamma_3/\partial N_3)_{N_2}$ similarly from eq. (5-13).

Since the mole fraction of component 3 in a ternary system is given by weight percent of each component as

$$N_3 = \frac{X_3}{M_3}\bigg/\left[\frac{100}{M_1}+\left(\frac{1}{M_2}-\frac{1}{M_1}\right)X_2+\left(\frac{1}{M_3}-\frac{1}{M_1}\right)X_3\right]$$

then

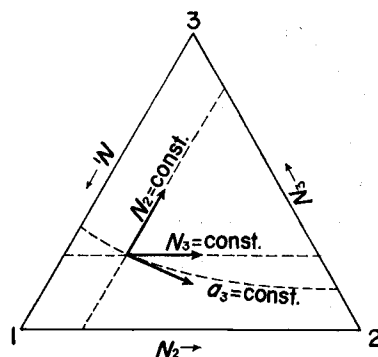$$X_3 = \frac{100M_3 + \left(\dfrac{M_1}{M_2} - 1\right)N_3 X_2}{\dfrac{M_1}{M_3} - \left(\dfrac{M_1}{M_3} - 1\right)N_3}$$

is obtained. As seen in this relation, it is clear that the line satisfying $N_3 =$ const. is represented by a straight line on weight percent coordinates generally not parallel to each weight percent axis. Then, as seen in eq. (6-21), two kinds of interaction parameters at constant weight percent, i.e. $(\partial \log f_3/\partial X_2)_{X_3}$, and $(\partial \log f_3/\partial X_3)_{X_2}$ are necessary in order to obtain an interaction parameter at constant mole fraction i.e. $(\partial \ln \gamma_3/\partial N_2)_{N_3}$ (Fig. 6).

Concerning eq. (5-18) in ternary system, it is sufficient to know only one interaction parameter at constant concentration ratio for the conversion calculation from the interaction parameter at constant mole fraction ratio to that at constant weight percent ratio or *vice versa*. It is clear that the above simple relation is due to the following equation:

$$\frac{X_1}{X_3} = \frac{N_1 M_3}{N_3 M_1} = \text{const},$$

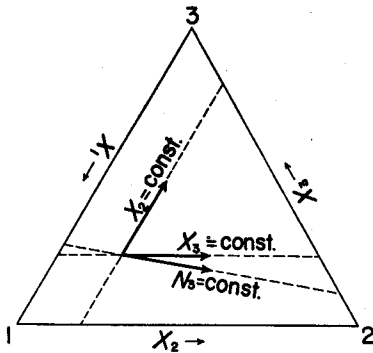i.e. when the ratio X_1/X_3 is constant, the ratio N_1/N_3 is also constant as shown in Fig. 7.

Fig. 6. Relation between interaction parameter at constant mole fraction and that at constant weight percent.
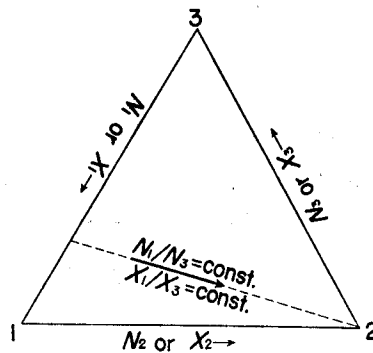
Fig. 7. Relation between interaction parameter at constant mole fraction ratio and that at constant weight percent ratio.

7. Relationship under Special Conditions

In the preceding sections, we have derived many equations which are applicable at any given concentration. These equations may be led to the comparatively simple forms, which had been already known, by imposing the special conditions (e.g. applying to infinite dilution).

In the case of infinitely dilute solution of all solutes, putting $N_s=0$; $s=2$, 3, $\cdots$, k in eq. (4–11), the following equation is derived:

$$\left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{N_l\,;\,l\neq 1,\,j} = \left(\frac{\partial \ln \gamma_j}{\partial N_i}\right)_{N_l\,;\,l\neq 1,\,i}, \quad \text{at} \quad N_s=0,\ s=2,3,\cdots,k. \tag{7-1}$$

This equation can be derived also from eq. (6–1) concerning termary alloys by putting $N_2=N_3=0$.

It follows that from the relation of eq. (6–5)

$$\left(\frac{\partial \ln \gamma_1}{\partial N_2}\right)_{N_1} = 0, \quad \text{at} \quad N_2=N_3=0. \tag{7-2}$$

This means that the activity of solvent 1, i.e. a_1 is in the range where Raoult's law is obeyed. On the contrary, if a_1 is in this range,

$$\left(\frac{\partial \ln \gamma_1}{\partial N_2}\right)_{N_3} = \left(\frac{\partial \ln \gamma_1}{\partial N_3}\right)_{N_2} = 0. \tag{7-3}$$

can also be proved, and therefore, from eqs. (6–2) and (6–3),

$$\left(\frac{\partial \ln \gamma_2}{\partial N_2}\right)_{N_3} N_2 + \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} N_3 = 0 \tag{7-4}$$

and

$$\left(\frac{\partial \ln \gamma_2}{\partial N_3}\right)_{N_2} N_2 + \left(\frac{\partial \ln \gamma_3}{\partial N_3}\right)_{N_2} N_3 = 0 \tag{7-5}$$

are valid. The range where a_1 obeys Raoult's law may be at the vicinity of $N_1 \fallingdotseq 1$ and furthermore when the solution is ideal, Raoult's law is obeyed even for the whole concentration range i.e. $0 \leq N_1 \leq 1$. Hence, it is obvious that the condition $N_2=N_3=0$ is not a necessary but a sufficient one. The necessary and sufficient condition for it is given by the following determinant:

$$\begin{vmatrix} \left(\dfrac{\partial \ln \gamma_2}{\partial N_2}\right)_{N_3} & \left(\dfrac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} \\[2ex] \left(\dfrac{\partial \ln \gamma_2}{\partial N_3}\right)_{N_2} & \left(\dfrac{\partial \ln \gamma_3}{\partial N_3}\right)_{N_2} \end{vmatrix} = 0, \tag{7-6}$$

and this equation is rewritten as

$$\left(\frac{\partial \ln \gamma_2}{\partial N_3}\right)_{N_2}\left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} = \left(\frac{\partial \ln \gamma_2}{\partial N_2}\right)_{N_3}\left(\frac{\partial \ln \gamma_3}{\partial N_3}\right)_{N_2}. \tag{7-7}$$

Therefore, in the range where the activity of solvent obeys Raoult's law

$$\left(\frac{\partial \ln \gamma_2}{\partial N_3}\right)_{N_2} = \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} = \pm \sqrt{\left(\frac{\partial \ln \gamma_2}{\partial N_2}\right)_{N_3}\left(\frac{\partial \ln \gamma_3}{\partial N_3}\right)_{N_2}}. \tag{7-8}$$

Substitution of $X_s=0$: $s=2,3,\cdots,k$ in eq. (4–28) yields

$$\left(\frac{\partial \log f_i}{\partial X_j}\right)_{X_l \,;\, l \mp 1, j} = \frac{1}{230.3}\left[\left\{230.3\left(\frac{\partial \log f_j}{\partial X_i}\right)_{X_l \,;\, l \mp 1, i} - 1\right\}\frac{M_i}{M_j} + 1\right]$$
$$\text{at} \quad X_s = 0\,; \; s = 2, 3, \cdots, k\,. \tag{7-9}$$

This relation in ternary system has been derived by H. Schenck *et al.*[7] Upon combining eq. (7-9) and eq. (6-10), it follows that

$$\frac{1}{M_1}\left(\frac{\partial \log f_1}{\partial X_2}\right)_{X_s} = \frac{1}{230.3}\left(\frac{1}{M_3} - \frac{1}{M_2}\right). \tag{7-10}$$

Upon introduction of the condition $N_2 = N_3 = 0$ and eq. (7-3) into eq. (5-13), one obtains

$$\frac{1}{M_1}\left(\frac{\partial \log f_1}{\partial X_2}\right)_{X_s} = \frac{1}{230.3}\left(\frac{1}{M_1} - \frac{1}{M_2}\right) \tag{7-11}$$

and

$$\frac{1}{M_1}\left(\frac{\partial \log f_1}{\partial X_3}\right)_{X_2} = \frac{1}{230.3}\left(\frac{1}{M_1} - \frac{1}{M_3}\right). \tag{7-12}$$

Eqs. (7-10) to (7-12) show that the interaction parameter of solvent at constant weight percents on Henrian basis is not generally equal to zero where the activity a_1 obeys Raoult's law.

Relationship between interaction parameters at constant mole fractions and at constant weight percents in infinitely dilute solution is derived either from eq. (5-11), (5-13) or (5-15) as

$$\left(\frac{\partial \log f_i}{\partial X_j}\right)_{X_l, \, l \mp 1, j} = \frac{1}{230.3}\left[\left\{\left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{N_l \,;\, l \mp 1, j} - 1\right\}\frac{M_1}{M_j} + 1\right]. \tag{7-13}$$

This has been also derived by Schenck *et al.*[7]

Following equations are obtained from eqs. (5-33) or (5-37) and (5-38) or (5-42) in infinitely dilute solution:

$$\left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{N_l \,;\, l \mp 1, j} = \beta_i^{(j)}, \quad \text{at} \quad N_s = 0, \, s = 2, 3, \cdots, k, \tag{7-14}$$

$$\left(\frac{\partial \log f_i}{\partial X_j}\right)_{X_l \,;\, l \mp 1, j} = b_i^{(j)}, \quad \text{at} \quad X_s = 0, \, s = 2, 3, \cdots, k, \tag{7-15}$$

and

$$b_i^{(j)} = \frac{1}{230.3}\left[(\beta_i^{(j)} - 1)\frac{M_1}{M_j} + 1\right], \quad \text{at} \quad N_s = X_s = 0, \; s = 2, 3, \cdots, k\,. \tag{7-16}$$

In multicomponent solution, the relation between interaction parameters at constant concentration and at constant activity is generally represented from eq. (5-24) or (5-30) as

$$\sum_{\substack{s=2 \\ s \neq i}}^{k}\left(\frac{\partial \ln \gamma_i}{\partial N_s}\right)_{N_l \,;\, l \mp 1, s}\frac{1}{\varepsilon_i^{(s)} a} = 1, \quad \text{at} \quad N_i = 0 \tag{7-17}$$

or

$$\sum_{\substack{s=2 \\ s \neq i}}^{k} \left(\frac{\partial \log f_i}{\partial X_s}\right)_{X_l \,;\, l \neq 1, s} \frac{1}{e_i^{(s)} a} = 1, \quad \text{at} \quad X_i = 0. \tag{7-18}$$

Either of these equations becomes simple for a ternary alloy :[3),7),8)]

$$\varepsilon_3^{(2)} a = \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} \quad \text{at} \quad N_3 = 0, \tag{7-19}$$

or

$$e_3^{(2)} a = \left(\frac{\partial \log f_3}{\partial X_2}\right)_{X_3} \quad \text{at} \quad X_3 = 0. \tag{7-20}$$

It should be noted that in these equations, only $N_i = X_i = 0$ or $N_i = X_3 = 0$ is necessary condition and the concentration of other components can take any arbitrary value. Eqs. (7-17) to (7-20) are also valid for the condition where a_i or $a_i(\%)$ obeys Henry's law instead of the condition N_i or $X_i = 0$.

From the following relation given by substitution of eq. (5-16) in Maxwell cross differential eq. (4-10):

$$\beta_i^{(j)}(1 - N_j) = \beta_j^{(i)}(1 - N_i), \tag{7-21}$$

it is clear that

$$\beta_i^{(j)} = \beta_j^{(i)} \quad \text{at} \quad N_i = N_j \tag{7-22}$$

and it is not necessary to give the condition $N_i = N_j = 0$.[7)] From eqs. (6-1) and (4-19) in a ternary system,

$$\left(\frac{\partial \ln \gamma_2}{\partial N_2}\right)_{N_1} N_2 - \left(\frac{\partial \ln \gamma_2}{\partial N_3}\right)_{N_2} N_1 = \left(\frac{\partial \ln \gamma_3}{\partial N_3}\right)_{N_1} N_3 - \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_3} N_1 \tag{7-23}$$

is given, and imposing $N_1 = 0$ in this equation, one obtains

$$\left(\frac{\partial \ln \gamma_2}{\partial N_3}\right)_{N_1} N_2 = \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_1} N_3 . \tag{7-25}$$

Then, this yields

$$\left(\frac{\partial \ln \gamma_2}{\partial N_3}\right)_{N_1} = \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_1} \quad \text{at} \quad N_2 = N_3 = 0.5 . \tag{7-24}$$

The relation of eq. (4-20) was used to derive eq. (7-24), while it can be shown that eq. (7-25) is a special one eq. (7-22), as follows.

In a ternary system, eq. (7-22) becomes

$$\left(\frac{\partial \ln \gamma_2}{\partial N_3}\right)_{N_1/N_2} = \left(\frac{\partial \ln \gamma_3}{\partial N_2}\right)_{N_1/N_3} , \quad \text{at} \quad N_2 = N_3 \tag{7-26}$$

This relation illustrates that, in a ternary diagram (Fig. 8), the tangent of $\ln \gamma_2$ along the line P3 towards vertex 3 at the intersection point P which lies
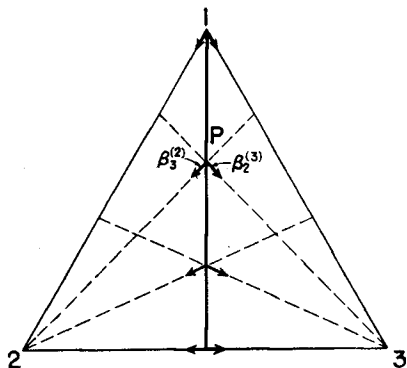
Fig. 8. The locus of the point satis-
fying the condition $\beta_3{}^{(2)}=\beta_2{}^{(3)}$ in
ternary system.

Fig. 9. The relation between activity
coefficient of Iron and Nickel and
their mole fractions in Fe-Ni alloys
at 1600°C.

on the line $N_2=N_3$ is equal to that of $\ln \gamma_3$ along the line P2 towards vertex 2 at the same point P. It is sure that eq. (7-26) satisfies both eqs. (7-1) and (7-25), because eq. (7-26) is valid under the condition $N_2=N_3$.

Eq. (7-24) has been derived from Maxwell cross differentials, while eq. (7-24) which can be derived from Gibbs-Duhem relation also yields this equation. Eq. (7-25) illustrates actually the relation concerning a binary system, because N_1 is equal to zero. Fig. 9 represents the relation between the activity coefficients of iron and nickel and their mole fractions taken from the data by R. Speiser, A. J. Jacobs and J. W. Spretnak.[10] Curves of $\log \gamma_{\mathrm{Fe}}$ and $\log \gamma_{\mathrm{Ni}}$ in this figure should satisfy eq. (7-25) at $N_{\mathrm{Fe}}=N_{\mathrm{Ni}}=0.5$, and calculation resulted the following value:

$$\frac{\partial \log \gamma_{\mathrm{Fe}}}{\partial N_{\mathrm{Ni}}} = \frac{\partial \log \gamma_{\mathrm{Ni}}}{\partial N_{\mathrm{Fe}}} \simeq -0.17. \tag{7-27}$$

Strictly speaking, however, for the experimental verification of eq. (7-25) more detailed data near $N_2=N_3=0.5$ may be required.

The relation of interaction parameters at constant weight percent ratio in infinitely dilute solution of component i and j is shown from eq. (4-41):

$$b_i^{(j)} = \frac{1}{230.3}\left[(230.3b_j^{(i)}-1)\frac{M_i}{M_j}+1\right]. \tag{7-28}$$

Although this relation requires the condition; $X_i=0$ and $X_j=0$, it is valid at

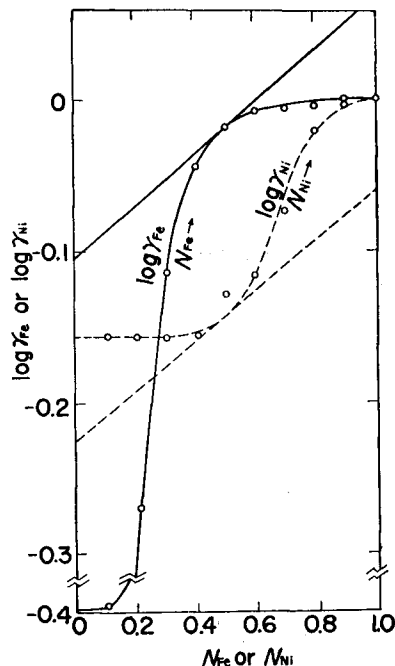any given concentration of the other components. When $M_i \simeq M_j$, eq. (7-28) becomes

$$b_j^{(i)} \simeq b_j^{(i)} \frac{M_i}{M_j}. \qquad (7\text{-}29)$$

Similar relation of this equation have been derived by J. Chipman[11] and by Schenck et al.[7]

Since the other relationship between interaction parameters concerning an infinitely dilute solution have been reported, we have here omitted discussing it.

Appendix A

On $\varepsilon_i^{(j)}$; the representation of interaction parameter at constant mole fractions

$\varepsilon_i^{(j)}$ has been defined by eq. (3-15). On the other hand, since there is a general relation (4-20);

$$\left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{N_2,N_3,\cdots,N_{j-1},N_{j+1},\cdots,N_k} = -\left(\frac{\partial \ln \gamma_i}{\partial N_1}\right)_{N_2,N_3,\cdots,N_{j-1},N_{j+1},\cdots,N_k}, \qquad (A\text{-}1)$$

then, according to the representation of eq. (3-15), we may represent this as

$$\varepsilon_i^{(j)} = -\varepsilon_i^{(1)}. \qquad (A\text{-}2)$$

In a similar manner, when $m \neq j$

$$\left(\frac{\partial \ln \gamma_i}{\partial N_m}\right)_{N_2,N_3,\cdots,N_{m-1},N_{m+1},\cdots,N_k} = -\left(\frac{\partial \ln \gamma_i}{\partial N_1}\right)_{N_2,N_3,\cdots,N_{m-1},N_{m+1},\cdots,N_k}, \qquad (A\text{-}3)$$

consequently

$$\varepsilon_i^{(m)} = -\varepsilon_i^{(1)} \qquad (A\text{-}4)$$

The right-hand side of eqs. (A-2) and (A-4) is identical as far as its symbol is concerned, hence it follows that

$$\varepsilon_i^{(j)} = \varepsilon_i^{(m)} \qquad (A\text{-}5)$$

However, as seen in eqs. (A-1) and (A-3), $\varepsilon_i^{(1)}$ in eq. (A-2) and that in eq. (A-4) are different from each other. The difference is illustrated in Fig. 10 concerning a ternary system.

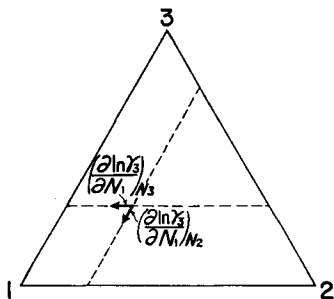Furthermore, it is not clear whether the symbol $\varepsilon_2^{(2)}$ indicates

Fig. 10. Comparison of $(\partial \ln \gamma_3/\partial N_1)_{N_3}$ and $(\partial \ln \gamma_3/\partial N_1)_{N_2}$.
There are two cases for the interaction parameter $\varepsilon_3^{(1)}$, and these are generally not equal to each other.

$$\varepsilon_2^{(2)} = \left(\frac{\partial \ln \gamma_2}{\partial N_2}\right)_{N_1}, \tag{A-6}$$

or

$$\varepsilon_2^{(2)} = \left(\frac{\partial \ln \gamma_2}{\partial N_2}\right)_{N_3}. \tag{A-7}$$

That is to say, the introduction of the symbol $\varepsilon_i^{(j)}$ to the interaction parameter at constant mole fractions is liable to cause misunderstanding, because the kinds of component to be kept constant are not clear. Although we may promise that the condition at "constant" mole fractions does not include N_1, it would be difficult to determine what kind of component is chosen as the solvent N_1 in a highly concentrated solution.

Appendix B

It has been shown by Schenck *et al.*[3),7)] that the partial differentiation condition of constant number of moles is converted to that of constant mole fraction ratio at the differentiation with repect to mole fraction. Let us try to explain this condition qualitatively on ternary system.
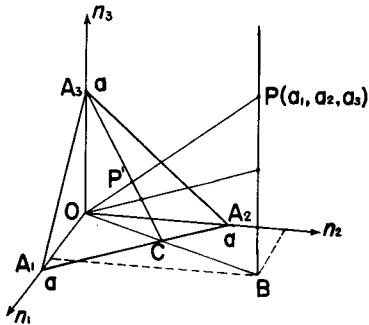
Consider three dimensional orthogonal co-ordinates having the axes of number of moles; n_1, n_2, n_3 (Fig. 11) The equation of the plane which intersects n_1, n_2 and n_3 axes at the point $A_1(a, 0, 0)$, $A_2(0, a, 0)$ and $A_3(0, 0, a)$ respectively is represented by

$$n_1 + n_2 + n_3 = a \tag{B-1}$$

While the straight line connecting from origin 0 to an arbitrary point $P(a_1, a_2, a_3)$ is given by

$$\frac{n_1}{a_1} = \frac{n_2}{a_2} = \frac{n_3}{a_3}. \tag{B-2}$$

Fig. 11. Relationship between the change of unmber of moles n_3 and that of mole fraction N_3 of component 3 in ternary system.

Then, these two equations give an intersection point P' of the plane $A_1A_2A_3$ and the straight line OP;

$$n_1 = \frac{aa_1}{a_1 + a_2 + a_3}, \quad n_2 = \frac{aa_2}{a_1 + a_2 + a_3}, \quad n_3 = \frac{aa_3}{a_1 + a_2 + a_3}. \tag{B-2}$$

Hence, putting $a = 1$, they represent the mole fractions corresponding to P. That is to say, the co-ordinates of the intersection point P' of the plane $A_1A_2A_3$

and the straight line OP represent the mole fractions of P.

Since $n_1 = $const. and $n_2 = $const. give an intersection line of each plane, this is represented by the line BP virtical to $n_1 - n_2$ plane. Connecting line from origin to the point on this vertical line BP lies on the plane including both n_3 axis and the line BP, thus the intersection line is A_3C on the plane $A_1A_2A_3$.

The line BP which means the condition where $n_3 = $variable, and n_1 and $n_2 = $constant corresponds to the line A_3C on the plane $A_1A_2A_3$ which means the condition of constant mole fraction ratio: N_1/N_2.

Now, let us choose the weight of each component; w_1, w_2, w_3 as the coordinate axes instead of number of moles. Then, using the plane intersecting each axis at $(100, 0, 0)$, $(0, 100, 0)$ and $(0, 0, 100)$, and considering that a constant number of moles of each component is identical with a constant weight of it, it can be readily shown that the derivative with respect to n_3 under the condition of $n_1 = $const. and $n_2 = $const. corresponds to that with respect to weight percent of the component 3 under the constant weight percent ratio of the component 1 and 2.

Appedix C

Since $N_j - N_j{}^\circ$ in eq. (3-25) is essentially a small quantity, we may express it as $\varDelta N_j$. Then eq. (3-25) may be rewritten as

$$\ln \gamma_i = \gamma_i{}^\circ + \sum_{j=1}^{k} \beta_i^{(j)}(1 - N_j{}^\circ)\varDelta N_j . \tag{C-1}$$

On the other hand, from eq. (2-2),

$$\sum_{j=1}^{k} \varDelta N_j = 0 , \tag{C-2}$$

then, one obtains

$$\varDelta N_1 = -\sum_{j=2}^{k} \varDelta N_j . \tag{C-3}$$

Substitution of eq. (C-3) in eq. (C-1) yields

$$\ln \gamma_i = \ln \gamma_i{}^\circ + \sum_{j=2}^{k} [\beta_i^{(j)}(1 - N_j{}^\circ) - \beta_i^{(1)}(1 - N_1{}^\circ)]\varDelta N_j . \tag{C-4}$$

Upon comparison of this equation with the following equation derived from eq. (3-2):

$$\ln \gamma_i = \ln \gamma_i{}^\circ + \sum_{j=2}^{k} \left(\frac{\partial \ln \gamma_i}{\partial N_j} \right)_{N_l\,;\,l\neq 1,\,j} \varDelta N_j , \tag{C-5}$$

it follows that

$$\left(\frac{\partial \ln \gamma_i}{\partial N_j}\right)_{N_l\,;\,l\,\neq\,1,\,j} = \beta_i^{(j)}(1-N_j{}^\circ)-\beta_i^{(1)}(1-N_1{}^\circ)\,. \tag{C-6}$$

This is the same relation as eq. (5-37).

Eq. (5-42) can be also derived in a similar manner.

Summary

The general relationship between activities and activity coefficients based on Raoultian and Henrian reference states substantiated at any given concentration was derived in a different aspect. It was shown that the theoretical series expansion of Wagner type using interaction parameters at constant concentration is possible even in any concentrated solution. It was also demonstrated that Taylor series expansion of logarithm of activity coefficient using interaction parameters at constant concentration ratio is possible. The conversion equations between several kinds of interaction parameters which are valid at any given concentration were derived. It may be said that these relations give usefull means to the thermodynomic investigation on multi-component alloys.

The interaction parameter at constant concentration, e.g. $(\partial \ln \gamma_i/\partial N_j)_{N_l\,;\,l\,\neq\,1,\,j}$ or $(\partial \log f_i/\partial X_j)_{X_l\,;\,l\,\neq\,1,\,j}$, is, in general, somewhat troublesome to be converted to $(\partial \ln \gamma_j/\partial N_i)_{N_l\,;\,l\,\neq\,1,\,i}$ or $(\partial \log f_j/\partial X_i)_{X_l\,;\,l\,\neq\,1,\,i}$ at high concentration of solute as seen in eq. (4-11) or eq. (4-27), and therefore either of these is more or less inconvenient to use. On the other hand, the interaction parameters at constant concentration ratio are readily converted to each other as seen in eq. (6-11) or (6-12), and moreover, these parameters may be easier to measure than those at constant concentration, because the experiments can be performed merely by adding the solute i to any given solution.

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