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The stability condition of phase equilibrium for various concentration variables

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The stability conditions of phase equilibrium for various concentration variables are educed according to thermodynamic principle. When a system with k components arrives at stable equilibrium, if the mole number n_i or the mole fraction $y_i(= n_i/n_k)$ or molality $m_i[= n_i/(n_k M_k)]$ of component i $(i = 1, 2, \ldots, k-1)$ are elected as concentration variables, thermodynamic theory is able to confirm that the sign of every order determinant composed of the second-order partial differential of chemical potential with respect to these concentration variables is positive; if the mole fraction $x_i(= n_i/n)$ or mass fraction $w_i(= n_i M_i/W)$ are elected as the concentration variables, thermodynamic theory is only able to confirm that the sign of $(k-1)$ order determinant is positive; if molarity $c_i(= n_i/V)$ are elected as the concentration variables, thermodynamic theory is not able to confirm the sign of every order determinant.

KEY WORDS: phase equilibrium, stability condition

1. Introduction

We know that there are four kinds of equilibriums in thermodynamics: thermal equilibrium, mechanical equilibrium, phase equilibrium and chemical equilibrium. Correspondingly there are four kinds of equilibrium conditions and four kinds of the stability conditions of equilibrium. At present we only discuss the stability condition of phase equilibrium. The form of the stability condition of phase equilibrium is different with the difference of concentration variables elected. Now we educe the stability condition of phase equilibrium for various concentration variables according to thermodynamic principle. They have obtained important application in thermodynamic theory of multi-component phase equilibrium [1–5].

2. The stability condition of phase equilibrium for various concentration variables

Supposing that there are k components and φ phases in a closed system without adiabatic walls, rigid walls, semi-permeable walls and curved interfaces, and chemical potential and mole number of various component in the system is μ and n, respectively. Therefore *Gibbs* free energy G in the system is

$$G = \sum_{\sigma=1}^{\varphi} \sum_{i=1}^{k} n_i^{(\sigma)} \mu_i^{(\sigma)}. \tag{1}$$

The condition of closed system is

$$\sum_{\sigma=1}^{\varphi} n_i^{(\sigma)} = n_i = \text{constant} \quad (i = 1,\ 2, \ldots, k). \tag{2}$$

To find the stability condition of phase equilibrium is just to find the sufficient condition to make G minimum under isothermic and isobaric condition as well as restrictive condition (2). Differentiating equation (1), we obtain

$$\mathrm{d}G = \sum_{\sigma=1}^{\varphi} \sum_{i=1}^{k} \mu_i^{(\sigma)} \mathrm{d}n_i^{(\sigma)} + \sum_{\sigma=1}^{\varphi} \sum_{i=1}^{k} n_i^{(\sigma)} \mathrm{d}\mu_i^{(\sigma)}. \tag{3}$$

Substituting *Gibbs–Duhem* formula

$$\sum_{i=1}^{k} n_i^{(\sigma)} \mathrm{d}\mu_i^{(\sigma)} = 0. \tag{4}$$

into equation (3), we obtain

$$\mathrm{d}G = \sum_{\sigma=1}^{\varphi} \sum_{i=1}^{k} \mu_i^{(\sigma)} \mathrm{d}n_i^{(\sigma)} = \sum_{\sigma=1}^{\varphi-1} \sum_{i=1}^{k} \mu_i^{(\sigma)} \mathrm{d}n_i^{(\sigma)} + \sum_{i=1}^{k} \mu_i^{(\varphi)} \mathrm{d}n_i^{(\varphi)}. \tag{5}$$

Differentiating equation (2), we obtain

$$\sum_{\sigma=1}^{\varphi} \mathrm{d}n_i^{(\sigma)} = 0 \quad \text{or} \quad \mathrm{d}n_i^{(\varphi)} = -\sum_{\sigma=1}^{\varphi-1} \mathrm{d}n_i^{(\sigma)}. \tag{6}$$

Substituting equation (6) into equation (5), we obtain

$$\mathrm{d}G = \sum_{\sigma=1}^{\varphi-1} \sum_{i=1}^{k} [\mu_i^{(\sigma)} - \mu_i^{(\varphi)}] \mathrm{d}n_i^{(\sigma)}. \tag{7}$$

When the system arrives at equilibrium, we have

$$\mathrm{d}G = \sum_{\sigma=1}^{\varphi-1} \sum_{i=1}^{k} [\mu_i^{(\sigma)} - \mu_i^{(\varphi)}] \mathrm{d}n_i^{(\sigma)} = 0. \tag{8}$$

We obtain by equation (8)

$$\mu_i^{(\sigma)} = \mu_i^{\varphi} \quad (i = 1,\ 2, \ldots, k, \sigma = 1,\ 2, \ldots, \varphi - 1). \tag{9}$$

Equation (9) is just the necessary condition of phase equilibrium. Now we find the sufficient condition of phase equilibrium, namely the stability condition of phase equilibrium. Differentiating equation (7), we obtain

$$\mathrm{d}^2 G = \sum_{\sigma=1}^{\varphi-1} \sum_{i=1}^{k} [\mathrm{d}\mu_i^{(\sigma)} - \mathrm{d}\mu_i^{(\varphi)}]\mathrm{d}n_i^{(\sigma)} + \sum_{\sigma=1}^{\varphi-1} \sum_{i=1}^{k} [\mu_i^{(\sigma)} - \mu_i^{(\varphi)}]\mathrm{d}^2 n_i^{(\sigma)}. \tag{10}$$

Substituting equation (9) into equation (10), we obtain

$$\mathrm{d}^2 G = \sum_{\sigma=1}^{\varphi-1} \sum_{i=1}^{k} [\mathrm{d}\mu_i^{(\sigma)} - \mathrm{d}\mu_i^{(\varphi)}]\mathrm{d}n_i^{(\sigma)} = \sum_{\sigma=1}^{\varphi-1} \sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)}\mathrm{d}n_i^{(\sigma)} - \sum_{i=1}^{k} \mathrm{d}\mu_i^{(\varphi)} \sum_{\sigma=1}^{\varphi-1} \mathrm{d}n_i^{(\sigma)}. \tag{11}$$

Substituting equation (6) into equation (11), we obtain

$$\begin{aligned}
\mathrm{d}^2 G &= \sum_{\sigma=1}^{\varphi-1} \sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)}\mathrm{d}n_i^{(\sigma)} + \sum_{i=1}^{k} \mathrm{d}\mu_i^{(\varphi)}\mathrm{d}n_i^{(\varphi)} \\
&= \sum_{\sigma=1}^{\varphi} \sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)}\mathrm{d}n_i^{(\sigma)} = \sum_{\sigma=1}^{\varphi} \sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)}\mathrm{d}\left[x_i^{(\sigma)} n^{(\sigma)}\right] \\
&= \sum_{\sigma=1}^{\varphi} \sum_{i=1}^{k} x_i^{(\sigma)}\mathrm{d}\mu_i^{(\sigma)}\mathrm{d}n^{(\sigma)} + \sum_{\sigma=1}^{\varphi} n^{(\sigma)} \sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)}\mathrm{d}x_i^{(\sigma)} \\
&= \sum_{\sigma=1}^{\varphi} \frac{\mathrm{d}n^{(\sigma)}}{n^{\sigma}} \sum_{i=1}^{k} n_i^{\sigma}\mathrm{d}\mu_i^{(\sigma)} + \sum_{\sigma=1}^{\varphi} n^{(\sigma)} \sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)}\mathrm{d}x_i^{(\sigma)},
\end{aligned} \tag{12}$$

where $x_i^{\sigma} \left(= n_i^{\sigma} / n^{\sigma}\right)$ is the mole fraction of substance i in σ phase. Substituting equation (4) into equation (12), we obtain

$$\mathrm{d}^2 G = \sum_{\sigma=1}^{\varphi} n^{(\sigma)} \sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)}\mathrm{d}x_i^{(\sigma)}, \tag{13}$$

when the system arrives at stable equilibrium, we have $\mathrm{d}^2 G > 0$, viz.

$$\sum_{\sigma=1}^{\varphi} n^{(\sigma)} \sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)}\mathrm{d}x_i^{(\sigma)} > 0. \tag{14}$$

By equation (13) we know that the second order differential of G only depends on the differential of intensive property $\mu_i^{(\sigma)}$ and $x_i^{(\sigma)}$, and is independent of the differential of extensive property $n^{(\sigma)}$. This means that the sufficient condition of stable phase equilibrium only depends on intensive property. By equation (9) we know that the necessary condition of phase equilibrium only depends on intensive property too. Hence the magnitude of $n^{(\sigma)}$ do not affect phase equilibrium. So we suppose that $n^{(\sigma)}$ is constant, thus equation (6) becomes

$$\sum_{\sigma=1}^{\varphi} \mathrm{d}n_i^{(\sigma)} = \sum_{\sigma=1}^{\varphi} \mathrm{d}[x_i^{(\sigma)} n^{\sigma}] = \sum_{\sigma=1}^{\varphi} n^{\sigma} \mathrm{d}x_i^{(\sigma)} = 0. \tag{15}$$

Owing to restricted by equation (15), the differentials in equation (14) are not all independent. It is very difficult that if we eliminate dependent differentials in equation (14) by equation (15). Therefore we must look for other method to avoid this difficulty. Now we prove that if equation (14) is tenable, then no doubt we have

$$\sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)} \mathrm{d}x_i^{(\sigma)} \geqslant 0 \quad (\text{For all } \sigma), \tag{16}$$

where $\sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)} \mathrm{d}x_i^{(\sigma)}$ is not all equal to 0 for σ. Supposing equation (16) is not tenable for a certain phase or some phases, viz. $\sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)} \mathrm{d}x_i^{(\sigma)} < 0$, then we may make $n^{(\sigma)}$ enough big for this phase or these phases, and the rest $n^{(\sigma)}$ enough small, even approach 0 (but not equal to 0, otherwise the number of phase is φ no more). $n^{(\sigma)}$ is extensive property, its magnitude does not affect phase equilibrium, phase equilibrium is decided by intensive property. $\sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)} \mathrm{d}x_i^{(\sigma)}$ is intensive property, it does not change with $n^{(\sigma)}$. After $n^{(\sigma)}$ is selected in this way, the sign of $\sum_{\sigma=1}^{\varphi} n^{(\sigma)} \sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)} \mathrm{d}x_i^{(\sigma)}$ is determined by $\sum_{i=1}^{k} \mathrm{d}\mu_i^{(\sigma)} \mathrm{d}x_i^{(\sigma)}$ with negative value, thus equation (14) is not tenable. In this way we have proved the validity of equation (16). Now we may disregard the interphase concentrations restrictive condition equation (15).

Thereinafter we only consider inequality in equation (16), and ignore right superscript σ:

$$\sum_{i=1}^{k} \mathrm{d}\mu_i \, \mathrm{d}x_i > 0. \tag{17}$$

2.1. The stability condition of phase equilibrium for concentration variables n_i

Although we may disregard the interphase concentration restrictive condition, we need to consider the inphase concentration restrictive condition yet. The number of the inphase independent concentration variables is $k-1$. Now we eliminate dependent concentration variables in equation (17). Due to

$$\sum_{i=1}^{k} \mathrm{d}\mu_i \mathrm{d}x_i = \sum_{i=1}^{k-1} \mathrm{d}\mu_i \, \mathrm{d}x_i + \mathrm{d}\mu_k \, \mathrm{d}x_k. \tag{18}$$

We define a new concentration variable

$$y_i = \frac{n_i}{n_k} = \frac{x_i}{x_k} \quad \text{or} \quad x_i = x_k y_i \ \ (i = 1,\ 2, \ldots, k-1). \tag{19}$$

Apparently $y_k = 1$. Substituting equation (19) into equation (18), we obtain

$$\begin{aligned} \sum_{i=1}^{k} \mathrm{d}\mu_i\, \mathrm{d}x_i &= x_k \sum_{i=1}^{k-1} \mathrm{d}\mu_i\, \mathrm{d}y_i + \sum_{i=1}^{k-1} y_i \mathrm{d}\mu_i\, \mathrm{d}x_k + \mathrm{d}\mu_k\, \mathrm{d}x_k \\ &= x_k \sum_{i=1}^{k-1} \mathrm{d}\mu_i\, dy_i + \sum_{i=1}^{k} y_i \mathrm{d}\mu_i\, \mathrm{d}x_k \\ &= x_k \sum_{i=1}^{k-1} \mathrm{d}\mu_i\, \mathrm{d}y_i + \frac{\mathrm{d}x_k}{x_k} \sum_{i=1}^{k} x_i \mathrm{d}\mu_i = x_k \sum_{i=1}^{k-1} \mathrm{d}\mu_i \mathrm{d}y_i. \end{aligned} \tag{20}$$

Again

$$\mathrm{d}\mu_i = \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}n_j = \sum_{j=1}^{k-1} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}n_j + \frac{\partial \mu_i}{\partial n_k} \mathrm{d}n_k. \tag{21}$$

By equation (19) we obtain

$$n_j = n_k y_j \quad (j = 1,\ 2, \ldots, k-1). \tag{22}$$

Substituting equation (22) into equation (21), we obtain

$$\begin{aligned} \mathrm{d}\mu_i &= n_k \sum_{j=1}^{k-1} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}y_j + \sum_{j=1}^{k-1} y_j \frac{\partial \mu_i}{\partial n_j} \mathrm{d}n_k + \frac{\partial \mu_i}{\partial n_k} \mathrm{d}n_k \\ &= n_k \sum_{j=1}^{k-1} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}y_j + \sum_{j=1}^{k} y_j \frac{\partial \mu_i}{\partial n_j} \mathrm{d}n_k \\ &= n_k \sum_{j=1}^{k-1} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}y_j + \frac{\mathrm{d}n_k}{n_k} \sum_{j=1}^{k} n_j \frac{\partial \mu_i}{\partial n_j} = n_k \sum_{j=1}^{k-1} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}y_j. \end{aligned} \tag{23}$$

Substituting equation (23) into equation (20), and taking note of equation (17), we obtain

$$\sum_{i=1}^{k} \mathrm{d}\mu_i\, \mathrm{d}x_i = n_k x_k \sum_{i=1}^{k-1} \sum_{j=1}^{k-1} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}y_j\, \mathrm{d}y_i > 0. \tag{24}$$

By Higher Algebra we know that if equation (24) is tenable, there are must

$$\begin{vmatrix} \frac{\partial \mu_1}{\partial n_1} & \frac{\partial \mu_1}{\partial n_2} & \cdots & \frac{\partial \mu_1}{\partial n_l} \\ \frac{\partial \mu_2}{\partial n_1} & \frac{\partial \mu_2}{\partial n_2} & \cdots & \frac{\partial \mu_2}{\partial n_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial n_1} & \frac{\partial \mu_l}{\partial n_2} & \cdots & \frac{\partial \mu_l}{\partial n_l} \end{vmatrix} > 0 \quad (l = 1,\ 2, \ldots, k-1). \tag{25}$$

Equation (25) is just the stability condition of phase equilibrium for concentration variables n_i. Because every component may be regarded as the first component, by equation (25) we obtain

$$\frac{\partial \mu_i}{\partial n_i} > 0 \quad (i = 1,\ 2, \ldots, k) \tag{26}$$

But equation (25) can not be replaced by equation (26).

2.2. *The stability condition of phase equilibrium for concentration variables y_i*

By equation (24) we know that n_k is always fixed for the partial differential of μ_i with respect to n_j. So by equation (22) we obtain

$$\partial n_j = n_k \partial y_j \quad (j = 1,\ 2, \ldots, k-1). \tag{27}$$

Substituting equation (27) into equation (25), we obtain

$$\begin{vmatrix} \frac{\partial \mu_1}{\partial y_1} & \frac{\partial \mu_1}{\partial y_2} & \cdots & \frac{\partial \mu_1}{\partial y_l} \\ \frac{\partial \mu_2}{\partial y_1} & \frac{\partial \mu_2}{\partial y_2} & \cdots & \frac{\partial \mu_2}{\partial y_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial y_1} & \frac{\partial \mu_l}{\partial y_2} & \cdots & \frac{\partial \mu_l}{\partial y_l} \end{vmatrix} > 0 \quad (l = 1,\ 2, \ldots, k-1). \tag{28}$$

Equation (28) is just the stability condition of phase equilibrium for concentration variables y_i. Because every component may be regarded as the first component, by equation (28) we obtain

$$\frac{\partial \mu_i}{\partial y_i} > 0 \quad (i = 1,\ 2, \ldots, k). \tag{29}$$

But equation (28) can not be replaced by equation (29).

2.3. The stability condition of phase equilibrium for concentration variables m_i

Molality m_i is defined as

$$m_i = \frac{n_i}{n_k M_k} = \frac{y_i}{M_k} \quad \text{or} \quad y_i = M_k m_i \quad (i = 1,\ 2, \ldots, k-1), \tag{30}$$

where M_k is mole weight of component k. Apparently $m_k = 1/M_k$. Substituting equation (30) into equation (28), we obtain

$$\begin{vmatrix} \frac{\partial \mu_1}{\partial m_1} & \frac{\partial \mu_1}{\partial m_2} & \cdots & \frac{\partial \mu_1}{\partial m_l} \\ \frac{\partial \mu_2}{\partial m_1} & \frac{\partial \mu_2}{\partial m_2} & \cdots & \frac{\partial \mu_2}{\partial m_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial m_1} & \frac{\partial \mu_l}{\partial m_2} & \cdots & \frac{\partial \mu_l}{\partial m_l} \end{vmatrix} > 0 \quad (l = 1,\ 2, \ldots, k-1). \tag{31}$$

Equation (31) is just the stability condition of phase equilibrium for concentration variables m_i. Because every component may be regarded as the first component, by equation (31) we obtain

$$\frac{\partial \mu_i}{\partial m_i} > 0 \quad (i = 1,\ 2, \ldots, k). \tag{32}$$

But equation (31) can not be replaced by equation (32).

2.4. The stability condition of phase equilibrium for concentration variables x_i

Owing to

$$\begin{aligned} \mathrm{d}\mu_i &= \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}n_j = \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}(x_j n) \\ &= \sum_{j=1}^{k} x_j \frac{\partial \mu_i}{\partial n_j} \mathrm{d}n + n \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}x_j \\ &= \frac{1}{n} \sum_{j=1}^{k} n_j \frac{\partial \mu_i}{\partial n_j} \mathrm{d}n + n \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}x_j \\ &= n \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}x_j = n \sum_{j=1}^{k-1} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}x_j + n \frac{\partial \mu_i}{\partial n_k} \mathrm{d}x_k \end{aligned}$$

$$= n\sum_{j=1}^{k-1}\frac{\partial\mu_i}{\partial n_j}\mathrm{d}x_j + n\frac{\partial\mu_i}{\partial n_k}\left(-\sum_{j=1}^{k-1}\mathrm{d}x_j\right)$$

$$= n\sum_{j=1}^{k-1}\left(\frac{\partial\mu_i}{\partial n_j} - \frac{\partial\mu_i}{\partial n_k}\right)\mathrm{d}x_j. \qquad (33)$$

By equation (33) we obtain

$$\frac{\partial\mu_i}{\partial x_j} = n\left(\frac{\partial\mu_i}{\partial n_j} - \frac{\partial\mu_i}{\partial n_k}\right) \quad (j = 1,\ 2, \ldots, k-1). \qquad (34)$$

By equation (34) we obtain

$$\begin{vmatrix} \frac{\partial\mu_1}{\partial x_1} & \frac{\partial\mu_1}{\partial x_2} & \cdots & \frac{\partial\mu_1}{\partial x_l} \\ \frac{\partial\mu_2}{\partial x_1} & \frac{\partial\mu_2}{\partial x_2} & \cdots & \frac{\partial\mu_2}{\partial x_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial x_1} & \frac{\partial\mu_l}{\partial x_2} & \cdots & \frac{\partial\mu_l}{\partial x_l} \end{vmatrix} = n^l \begin{vmatrix} \frac{\partial\mu_1}{\partial n_1} - \frac{\partial\mu_1}{\partial n_k} & \frac{\partial\mu_1}{\partial n_2} - \frac{\partial\mu_1}{\partial n_k} & \cdots & \frac{\partial\mu_1}{\partial n_l} - \frac{\partial\mu_1}{\partial n_k} \\ \frac{\partial\mu_2}{\partial n_1} - \frac{\partial\mu_2}{\partial n_k} & \frac{\partial\mu_2}{\partial n_2} - \frac{\partial\mu_2}{\partial n_k} & \cdots & \frac{\partial\mu_2}{\partial n_l} - \frac{\partial\mu_2}{\partial n_k} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial n_1} - \frac{\partial\mu_l}{\partial n_k} & \frac{\partial\mu_l}{\partial n_2} - \frac{\partial\mu_l}{\partial n_k} & \cdots & \frac{\partial\mu_l}{\partial n_l} - \frac{\partial\mu_l}{\partial n_k} \end{vmatrix}$$

(The first column multiplied by negative sign add to other column)

$$= n^l \begin{vmatrix} \frac{\partial\mu_1}{\partial n_1} - \frac{\partial\mu_1}{\partial n_k} & \frac{\partial\mu_1}{\partial n_2} - \frac{\partial\mu_1}{\partial n_1} & \cdots & \frac{\partial\mu_1}{\partial n_l} - \frac{\partial\mu_1}{\partial n_1} \\ \frac{\partial\mu_2}{\partial n_1} - \frac{\partial\mu_2}{\partial n_k} & \frac{\partial\mu_2}{\partial n_2} - \frac{\partial\mu_2}{\partial n_1} & \cdots & \frac{\partial\mu_2}{\partial n_l} - \frac{\partial\mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial n_1} - \frac{\partial\mu_l}{\partial n_k} & \frac{\partial\mu_l}{\partial n_2} - \frac{\partial\mu_l}{\partial n_1} & \cdots & \frac{\partial\mu_l}{\partial n_l} - \frac{\partial\mu_l}{\partial n_1} \end{vmatrix} \qquad (35)$$

Every component from $(l + 1)$ to k may be regarded as component k. So we change subscript k in determinant on the right of equation (35) into j, add subscript j to determinant on the left of equation (35) [to denote the value of the determinant related to choice of k], multiply two side of equation (35) by n_j, and then find sum from $(l + 1)$ to k:

$$\sum_{j=l+1}^{k} n_j \begin{vmatrix} \frac{\partial\mu_1}{\partial x_1} & \frac{\partial\mu_1}{\partial x_2} & \cdots & \frac{\partial\mu_1}{\partial x_l} \\ \frac{\partial\mu_2}{\partial x_1} & \frac{\partial\mu_2}{\partial x_2} & \cdots & \frac{\partial\mu_2}{\partial x_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial x_1} & \frac{\partial\mu_l}{\partial x_2} & \cdots & \frac{\partial\mu_l}{\partial x_l} \end{vmatrix}_j = n^l \sum_{j=l+1}^{k} n_j \begin{vmatrix} \frac{\partial\mu_1}{\partial n_1} - \frac{\partial\mu_1}{\partial n_j} & \frac{\partial\mu_1}{\partial n_2} - \frac{\partial\mu_1}{\partial n_1} & \cdots & \frac{\partial\mu_1}{\partial n_l} - \frac{\partial\mu_1}{\partial n_1} \\ \frac{\partial\mu_2}{\partial n_1} - \frac{\partial\mu_2}{\partial n_j} & \frac{\partial\mu_2}{\partial n_2} - \frac{\partial\mu_2}{\partial n_1} & \cdots & \frac{\partial\mu_2}{\partial n_l} - \frac{\partial\mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial n_1} - \frac{\partial\mu_l}{\partial n_j} & \frac{\partial\mu_l}{\partial n_2} - \frac{\partial\mu_l}{\partial n_1} & \cdots & \frac{\partial\mu_l}{\partial n_l} - \frac{\partial\mu_l}{\partial n_1} \end{vmatrix}$$

$$
= n^l \begin{vmatrix}
\sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_1}{\partial n_1} - \sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_1}{\partial n_j} & \dfrac{\partial \mu_1}{\partial n_2} - \dfrac{\partial \mu_1}{\partial n_1} & \cdots & \dfrac{\partial \mu_1}{\partial n_l} - \dfrac{\partial \mu_1}{\partial n_1} \\
\sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_2}{\partial n_1} - \sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_2}{\partial n_j} & \dfrac{\partial \mu_2}{\partial n_2} - \dfrac{\partial \mu_2}{\partial n_1} & \cdots & \dfrac{\partial \mu_2}{\partial n_l} - \dfrac{\partial \mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_l}{\partial n_1} - \sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_l}{\partial n_j} & \dfrac{\partial \mu_l}{\partial n_2} - \dfrac{\partial \mu_l}{\partial n_1} & \cdots & \dfrac{\partial \mu_l}{\partial n_l} - \dfrac{\partial \mu_l}{\partial n_1}
\end{vmatrix}
$$

$$
= n^l \begin{vmatrix}
\sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_1}{\partial n_1} + \sum\limits_{j=1}^{l} n_j \dfrac{\partial \mu_1}{\partial n_j} & \dfrac{\partial \mu_1}{\partial n_2} - \dfrac{\partial \mu_1}{\partial n_1} & \cdots & \dfrac{\partial \mu_1}{\partial n_l} - \dfrac{\partial \mu_1}{\partial n_1} \\
\sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_2}{\partial n_1} + \sum\limits_{j=1}^{l} n_j \dfrac{\partial \mu_2}{\partial n_j} & \dfrac{\partial \mu_2}{\partial n_2} - \dfrac{\partial \mu_2}{\partial n_1} & \cdots & \dfrac{\partial \mu_2}{\partial n_l} - \dfrac{\partial \mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_l}{\partial n_1} + \sum\limits_{j=1}^{l} n_j \dfrac{\partial \mu_l}{\partial n_j} & \dfrac{\partial \mu_l}{\partial n_2} - \dfrac{\partial \mu_l}{\partial n_1} & \cdots & \dfrac{\partial \mu_l}{\partial n_l} - \dfrac{\partial \mu_l}{\partial n_1}
\end{vmatrix}
$$

(Multiply column 2 by n_2, multiply column 3 by n_3, … multiply column l by n_l)

$$
= n^l \frac{1}{\prod\limits_{j=2}^{l} n_j} \begin{vmatrix}
\sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_1}{\partial n_1} + \sum\limits_{j=1}^{l} n_j \dfrac{\partial \mu_1}{\partial n_j} & n_2 \dfrac{\partial \mu_1}{\partial n_2} - n_2 \dfrac{\partial \mu_1}{\partial n_1} & \cdots & n_l \dfrac{\partial \mu_1}{\partial n_l} - n_l \dfrac{\partial \mu_1}{\partial n_1} \\
\sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_2}{\partial n_1} + \sum\limits_{j=1}^{l} n_j \dfrac{\partial \mu_2}{\partial n_j} & n_2 \dfrac{\partial \mu_2}{\partial n_2} - n_2 \dfrac{\partial \mu_2}{\partial n_1} & \cdots & n_l \dfrac{\partial \mu_2}{\partial n_l} - n_l \dfrac{\partial \mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\sum\limits_{j=l+1}^{k} n_j \dfrac{\partial \mu_l}{\partial n_1} + \sum\limits_{j=1}^{l} n_j \dfrac{\partial \mu_l}{\partial n_j} & n_2 \dfrac{\partial \mu_l}{\partial n_2} - n_2 \dfrac{\partial \mu_l}{\partial n_1} & \cdots & n_l \dfrac{\partial \mu_l}{\partial n_l} - n_l \dfrac{\partial \mu_l}{\partial n_1}
\end{vmatrix}
$$

(Every column multiplied by negative sign add to the first column)

$$
= n^l \frac{1}{\prod\limits_{j=2}^{l} n_j} \begin{vmatrix}
\sum\limits_{j=2}^{k} n_j \dfrac{\partial \mu_1}{\partial n_1} + n_1 \dfrac{\partial \mu_1}{\partial n_1} & n_2 \dfrac{\partial \mu_1}{\partial n_2} - n_2 \dfrac{\partial \mu_1}{\partial n_1} & \cdots & n_l \dfrac{\partial \mu_1}{\partial n_l} - n_l \dfrac{\partial \mu_1}{\partial n_1} \\
\sum\limits_{j=2}^{k} n_j \dfrac{\partial \mu_2}{\partial n_1} + n_1 \dfrac{\partial \mu_2}{\partial n_1} & n_2 \dfrac{\partial \mu_2}{\partial n_2} - n_2 \dfrac{\partial \mu_2}{\partial n_1} & \cdots & n_l \frac{\partial \mu_2}{\partial n_l} - n_l \dfrac{\partial \mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\sum\limits_{j=2}^{k} n_j \dfrac{\partial \mu_l}{\partial n_1} + n_1 \dfrac{\partial \mu_l}{\partial n_1} & n_2 \dfrac{\partial \mu_l}{\partial n_2} - n_2 \dfrac{\partial \mu_l}{\partial n_1} & \cdots & n_l \dfrac{\partial \mu_l}{\partial n_l} - n_l \dfrac{\partial \mu_l}{\partial n_1}
\end{vmatrix}
$$

$$
= n^l \begin{vmatrix}
\sum_{j=1}^{k} n_j \frac{\partial \mu_1}{\partial n_1} & \frac{\partial \mu_1}{\partial n_2} - \frac{\partial \mu_1}{\partial n_1} & \cdots & \frac{\partial \mu_1}{\partial n_l} - \frac{\partial \mu_1}{\partial n_1} \\
\sum_{j=1}^{k} n_j \frac{\partial \mu_2}{\partial n_1} & \frac{\partial \mu_2}{\partial n_2} - \frac{\partial \mu_2}{\partial n_1} & \cdots & \frac{\partial \mu_2}{\partial n_l} - \frac{\partial \mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\sum_{j=1}^{k} n_j \frac{\partial \mu_l}{\partial n_1} & \frac{\partial \mu_l}{\partial n_2} - \frac{\partial \mu_l}{\partial n_1} & \cdots & \frac{\partial \mu_l}{\partial n_l} - \frac{\partial \mu_l}{\partial n_1}
\end{vmatrix}
$$

$$
= n^{l+1} \begin{vmatrix}
\frac{\partial \mu_1}{\partial n_1} & \frac{\partial \mu_1}{\partial n_2} - \frac{\partial \mu_1}{\partial n_1} & \cdots & \frac{\partial \mu_1}{\partial n_l} - \frac{\partial \mu_1}{\partial n_1} \\
\frac{\partial \mu_2}{\partial n_1} & \frac{\partial \mu_2}{\partial n_2} - \frac{\partial \mu_2}{\partial n_1} & \cdots & \frac{\partial \mu_2}{\partial n_l} - \frac{\partial \mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{\partial \mu_l}{\partial n_1} & \frac{\partial \mu_l}{\partial n_2} - \frac{\partial \mu_l}{\partial n_1} & \cdots & \frac{\partial \mu_l}{\partial n_l} - \frac{\partial \mu_l}{\partial n_1}
\end{vmatrix}
$$

(The first column add to the other column)

$$
= n^{l+1} \begin{vmatrix}
\frac{\partial \mu_1}{\partial n_1} & \frac{\partial \mu_1}{\partial n_2} & \cdots & \frac{\partial \mu_1}{\partial n_l} \\
\frac{\partial \mu_2}{\partial n_1} & \frac{\partial \mu_2}{\partial n_2} & \cdots & \frac{\partial \mu_2}{\partial n_l} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{\partial \mu_l}{\partial n_1} & \frac{\partial \mu_l}{\partial n_2} & \cdots & \frac{\partial \mu_l}{\partial n_l}
\end{vmatrix} \tag{36}
$$

n divide into two side of equation (36):

$$
\sum_{j=l+1}^{k} x_j \begin{vmatrix}
\frac{\partial \mu_1}{\partial x_1} & \frac{\partial \mu_1}{\partial x_2} & \cdots & \frac{\partial \mu_1}{\partial x_l} \\
\frac{\partial \mu_2}{\partial x_1} & \frac{\partial \mu_2}{\partial x_2} & \cdots & \frac{\partial \mu_2}{\partial x_l} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{\partial \mu_l}{\partial x_1} & \frac{\partial \mu_l}{\partial x_2} & \cdots & \frac{\partial \mu_l}{\partial x_l}
\end{vmatrix}_j = n^l \begin{vmatrix}
\frac{\partial \mu_1}{\partial n_1} & \frac{\partial \mu_1}{\partial n_2} & \cdots & \frac{\partial \mu_1}{\partial n_l} \\
\frac{\partial \mu_2}{\partial n_1} & \frac{\partial \mu_2}{\partial n_2} & \cdots & \frac{\partial \mu_2}{\partial n_l} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{\partial \mu_l}{\partial n_1} & \frac{\partial \mu_l}{\partial n_2} & \cdots & \frac{\partial \mu_l}{\partial n_l}
\end{vmatrix}
\quad (l = 1,\ 2, \ldots, k-1) \tag{37}
$$

By equation (25) and equation (37) we obtain

$$\sum_{j=l+1}^{k} x_j \begin{vmatrix} \frac{\partial \mu_1}{\partial x_1} & \frac{\partial \mu_1}{\partial x_2} & \cdots & \frac{\partial \mu_1}{\partial x_l} \\ \frac{\partial \mu_2}{\partial x_1} & \frac{\partial \mu_2}{\partial x_2} & \cdots & \frac{\partial \mu_2}{\partial x_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial x_1} & \frac{\partial \mu_l}{\partial x_2} & \cdots & \frac{\partial \mu_l}{\partial x_l} \end{vmatrix}_j > 0 \qquad (l = 1,\ 2, \ldots, k-1) \qquad (38)$$

Equation (38) is just the stability condition of phase equilibrium for concentration variables x_i. The left of equation (38) is the sum of $(k - l)$ different determinant with l order. We are only able to confirm the sign of $(k - 1)$ order determinant in equation (38), because when $l = k - 1$, equation (38) becomes

$$\begin{vmatrix} \frac{\partial \mu_1}{\partial x_1} & \frac{\partial \mu_1}{\partial x_2} & \cdots & \frac{\partial \mu_1}{\partial x_{k-1}} \\ \frac{\partial \mu_2}{\partial x_1} & \frac{\partial \mu_2}{\partial x_2} & \cdots & \frac{\partial \mu_2}{\partial x_{k-1}} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_{k-1}}{\partial x_1} & \frac{\partial \mu_{k-1}}{\partial x_2} & \cdots & \frac{\partial \mu_{k-1}}{\partial x_{k-1}} \end{vmatrix} > 0. \qquad (39)$$

For example, for the solution composed of components A(1), B(2) and C(3), $k = 3$, $l = 1, 2$. If $l = 1$, equation (38) becomes

$$x_B \left(\frac{\partial \mu_A}{\partial x_A}\right)_B + x_C \left(\frac{\partial \mu_A}{\partial x_A}\right)_C > 0. \qquad (40)$$

For the first term in equation (40), B is regarded as component k, so

$$\mu_A = f(x_A,\ x_C), \quad \left(\frac{\partial \mu_A}{\partial x_A}\right)_B = \left(\frac{\partial \mu_A}{\partial x_A}\right)_{x_C}.$$

For the second term in equation (40), C is regarded as component k, so

$$\mu_A = f(x_A,\ x_B), \quad \left(\frac{\partial \mu_A}{\partial x_A}\right)_C = \left(\frac{\partial \mu_A}{\partial x_A}\right)_{x_B}.$$

Generally speaking, $\left(\frac{\partial \mu_A}{\partial x_A}\right)_{x_C} \neq \left(\frac{\partial \mu_A}{\partial x_A}\right)_{x_B}$, except for ideal gases or ideal solutions. If $l = 2$, equation (38) becomes

$$x_C \begin{vmatrix} \frac{\partial \mu_A}{\partial x_A} & \frac{\partial \mu_A}{\partial x_B} \\ \frac{\partial \mu_B}{\partial x_A} & \frac{\partial \mu_B}{\partial x_B} \end{vmatrix} > 0.$$

For ideal gases or ideal solutions, chemical potential of substance i only depend on mole fraction x_i of substance i. So for ideal gases or ideal solutions, determinant on the left of equation (38) is independent of x_j, thus equation (38) becomes

$$\begin{vmatrix} \frac{\partial \mu_1}{\partial x_1} & \frac{\partial \mu_1}{\partial x_2} & \cdots & \frac{\partial \mu_1}{\partial x_l} \\ \frac{\partial \mu_2}{\partial x_1} & \frac{\partial \mu_2}{\partial x_2} & \cdots & \frac{\partial \mu_2}{\partial x_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial x_1} & \frac{\partial \mu_l}{\partial x_2} & \cdots & \frac{\partial \mu_l}{\partial x_l} \end{vmatrix} \sum_{j=l+1}^{k} x_j > 0 \quad \text{or} \quad \begin{vmatrix} \frac{\partial \mu_1}{\partial x_1} & \frac{\partial \mu_1}{\partial x_2} & \cdots & \frac{\partial \mu_1}{\partial x_l} \\ \frac{\partial \mu_2}{\partial x_1} & \frac{\partial \mu_2}{\partial x_2} & \cdots & \frac{\partial \mu_2}{\partial x_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial x_1} & \frac{\partial \mu_l}{\partial x_2} & \cdots & \frac{\partial \mu_l}{\partial x_l} \end{vmatrix} > 0$$
$$(l = 1, 2, \ldots, k-1) \tag{41}$$

or

$$\begin{vmatrix} \frac{RT}{x_1} & 0 & \cdots & 0 \\ 0 & \frac{RT}{x_2} & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \frac{RT}{x_l} \end{vmatrix} = \frac{(RT)^l}{\prod_{i=1}^{l} x_i} > 0. \tag{42}$$

2.5. *The stability condition of phase equilibrium for concentration variables w_i*

Due to mass fraction $w_i = n_i M_i / W$ (W is the total mass of the system), so

$$\begin{aligned} \mathrm{d}\mu_i &= \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}n_j = \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}\left(\frac{w_j}{M_j} W\right) \\ &= \sum_{j=1}^{k} \frac{w_j}{M_j} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}W + \sum_{j=1}^{k} \frac{W}{M_j} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}w_j \\ &= \sum_{j=1}^{k} n_j \frac{\partial \mu_i}{\partial n_j} \frac{\mathrm{d}W}{W} + \sum_{j=1}^{k} \frac{W}{M_j} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}w_j \\ &= \sum_{j=1}^{k} \frac{W}{M_j} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}w_j \\ &= \sum_{j=1}^{k-1} \frac{W}{M_j} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}w_j + \frac{W}{M_k} \frac{\partial \mu_i}{\partial n_k} \mathrm{d}w_k \end{aligned}$$

$$= \sum_{j=1}^{k-1} \frac{W}{M_j} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}w_j - \frac{W}{M_k} \frac{\partial \mu_i}{\partial n_k} \sum_{j=1}^{k-1} \mathrm{d}w_j$$

$$= W \sum_{j=1}^{k-1} \left(\frac{1}{M_j} \frac{\partial \mu_i}{\partial n_j} - \frac{1}{M_k} \frac{\partial \mu_i}{\partial n_k} \right) \mathrm{d}w_j \qquad (43)$$

By equation (43) we obtain

$$\frac{\partial \mu_i}{\partial w_j} = W \left(\frac{1}{M_j} \frac{\partial \mu_i}{\partial n_j} - \frac{1}{M_k} \frac{\partial \mu_i}{\partial n_k} \right) \quad (j = 1,\ 2, \ldots, k-1) \qquad (44)$$

So

$$\begin{vmatrix} \frac{\partial \mu_1}{\partial w_1} & \frac{\partial \mu_1}{\partial w_2} & \cdots & \frac{\partial \mu_1}{\partial w_l} \\ \frac{\partial \mu_2}{\partial w_1} & \frac{\partial \mu_2}{\partial w_2} & \cdots & \frac{\partial \mu_2}{\partial w_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial w_1} & \frac{\partial \mu_l}{\partial w_2} & \cdots & \frac{\partial \mu_l}{\partial w_l} \end{vmatrix}$$

$$= W^l \begin{vmatrix} \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} - \frac{1}{M_k}\frac{\partial \mu_1}{\partial n_k} & \frac{1}{M_2}\frac{\partial \mu_1}{\partial n_2} - \frac{1}{M_k}\frac{\partial \mu_1}{\partial n_k} & \cdots & \frac{1}{M_l}\frac{\partial \mu_1}{\partial n_l} - \frac{1}{M_k}\frac{\partial \mu_1}{\partial n_k} \\ \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} - \frac{1}{M_k}\frac{\partial \mu_2}{\partial n_k} & \frac{1}{M_2}\frac{\partial \mu_2}{\partial n_2} - \frac{1}{M_k}\frac{\partial \mu_2}{\partial n_k} & \cdots & \frac{1}{M_l}\frac{\partial \mu_2}{\partial n_l} - \frac{1}{M_k}\frac{\partial \mu_2}{\partial n_k} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} - \frac{1}{M_k}\frac{\partial \mu_l}{\partial n_k} & \frac{1}{M_2}\frac{\partial \mu_l}{\partial n_2} - \frac{1}{M_k}\frac{\partial \mu_l}{\partial n_k} & \cdots & \frac{1}{M_l}\frac{\partial \mu_l}{\partial n_l} - \frac{1}{M_k}\frac{\partial \mu_l}{\partial n_k} \end{vmatrix}$$

(The first column multiplied by negative sign add to other column)

$$= W^l \begin{vmatrix} \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} - \frac{1}{M_k}\frac{\partial \mu_1}{\partial n_k} & \frac{1}{M_2}\frac{\partial \mu_1}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_1}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} \\ \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} - \frac{1}{M_k}\frac{\partial \mu_2}{\partial n_k} & \frac{1}{M_2}\frac{\partial \mu_2}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_2}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} - \frac{1}{M_k}\frac{\partial \mu_l}{\partial n_k} & \frac{1}{M_2}\frac{\partial \mu_l}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_l}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} \end{vmatrix} \qquad (45)$$

Every component from $(l+1)$ to k may be regarded as component k. So we change subscript k in determinant on the right of equation (45) into j, add subscript j to determinant on the left equation (45), multiply two side of equation

(45) by $n_j M_j$, and then find sum from $(l+1)$ to k:

$$\sum_{j=l+1}^{k} n_j M_j \begin{vmatrix} \frac{\partial \mu_1}{\partial w_1} & \frac{\partial \mu_1}{\partial w_2} & \cdots & \frac{\partial \mu_1}{\partial w_l} \\ \frac{\partial \mu_2}{\partial w_1} & \frac{\partial \mu_2}{\partial w_2} & \cdots & \frac{\partial \mu_2}{\partial w_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial w_1} & \frac{\partial \mu_l}{\partial w_2} & \cdots & \frac{\partial \mu_l}{\partial w_l} \end{vmatrix}_j$$

$$= W^l \sum_{j=l+1}^{k} n_j M_j \begin{vmatrix} \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} - \frac{1}{M_j}\frac{\partial \mu_1}{\partial n_j} & \frac{1}{M_2}\frac{\partial \mu_1}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_1}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} \\ \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} - \frac{1}{M_j}\frac{\partial \mu_2}{\partial n_j} & \frac{1}{M_2}\frac{\partial \mu_2}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_2}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} - \frac{1}{M_j}\frac{\partial \mu_l}{\partial n_j} & \frac{1}{M_2}\frac{\partial \mu_l}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_l}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} \end{vmatrix}$$

$$= W^l \begin{vmatrix} \sum_{j=l+1}^{k} n_j M_j \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} - \sum_{j=l+1}^{k} n_j \frac{\partial \mu_1}{\partial n_j} & \frac{1}{M_2}\frac{\partial \mu_1}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_1}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} \\ \sum_{j=l+1}^{k} n_j M_j \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} - \sum_{j=l+1}^{k} n_j \frac{\partial \mu_2}{\partial n_j} & \frac{1}{M_2}\frac{\partial \mu_2}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_2}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \sum_{j=l+1}^{k} n_j M_j \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} - \sum_{j=l+1}^{k} n_j \frac{\partial \mu_l}{\partial n_j} & \frac{1}{M_2}\frac{\partial \mu_l}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_l}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} \end{vmatrix}$$

$$= W^l \begin{vmatrix} \sum_{j=l+1}^{k} n_j M_j \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} + \sum_{j=1}^{l} n_j \frac{\partial \mu_1}{\partial n_j} & \frac{1}{M_2}\frac{\partial \mu_1}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_1}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_1}{\partial n_1} \\ \sum_{j=l+1}^{k} n_j M_j \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} + \sum_{j=1}^{l} n_j \frac{\partial \mu_2}{\partial n_j} & \frac{1}{M_2}\frac{\partial \mu_2}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_2}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \sum_{j=l+1}^{k} n_j M_j \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} + \sum_{j=1}^{l} n_j \frac{\partial \mu_l}{\partial n_j} & \frac{1}{M_2}\frac{\partial \mu_l}{\partial n_2} - \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial \mu_l}{\partial n_l} - \frac{1}{M_1}\frac{\partial \mu_l}{\partial n_1} \end{vmatrix}$$

(Multiply column 2 by n_2M_2, multiply column 3 by n_3M_3, … multiply column l by n_lM_l)

$$= \frac{W^l}{\prod_{j=2}^{l} n_jM_j}\begin{vmatrix} \frac{\sum_{j=l+1}^{k} n_jM_j}{M_1}\frac{\partial\mu_1}{\partial n_1} + \sum_{j=1}^{l} n_j\frac{\partial\mu_1}{\partial n_j} & n_2\frac{\partial\mu_1}{\partial n_2} - \frac{n_2M_2}{M_1}\frac{\partial\mu_1}{\partial n_1} & \cdots & n_l\frac{\partial\mu_1}{\partial n_l} - \frac{n_lM_l}{M_1}\frac{\partial\mu_1}{\partial n_1} \\ \frac{\sum_{j=l+1}^{k} n_jM_j}{M_1}\frac{\partial\mu_2}{\partial n_1} + \sum_{j=1}^{l} n_j\frac{\partial\mu_2}{\partial n_j} & n_2\frac{\partial\mu_2}{\partial n_2} - \frac{n_2M_2}{M_1}\frac{\partial\mu_2}{\partial n_1} & \cdots & n_l\frac{\partial\mu_2}{\partial n_l} - \frac{n_lM_l}{M_1}\frac{\partial\mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\sum_{j=l+1}^{k} n_jM_j}{M_1}\frac{\partial\mu_l}{\partial n_1} + \sum_{j=1}^{l} n_j\frac{\partial\mu_l}{\partial n_j} & n_2\frac{\partial\mu_l}{\partial n_2} - \frac{n_2M_2}{M_1}\frac{\partial\mu_l}{\partial n_1} & \cdots & n_l\frac{\partial\mu_l}{\partial n_l} - \frac{n_lM_l}{M_1}\frac{\partial\mu_l}{\partial n_1} \end{vmatrix}$$

(Every column multiplied by negative sign add to the first column)

$$= \frac{W^l}{\prod_{j=2}^{l} n_jM_j}\begin{vmatrix} \frac{\sum_{j=2}^{k} n_jM_j}{M_1}\frac{\partial\mu_1}{\partial n_1} + n_1\frac{\partial\mu_1}{\partial n_1} & n_2\frac{\partial\mu_1}{\partial n_2} - \frac{n_2M_2}{M_1}\frac{\partial\mu_1}{\partial n_1} & \cdots & n_l\frac{\partial\mu_1}{\partial n_l} - \frac{n_lM_l}{M_1}\frac{\partial\mu_1}{\partial n_1} \\ \frac{\sum_{j=2}^{k} n_jM_j}{M_1}\frac{\partial\mu_2}{\partial n_1} + n_1\frac{\partial\mu_2}{\partial n_1} & n_2\frac{\partial\mu_2}{\partial n_2} - \frac{n_2M_2}{M_1}\frac{\partial\mu_2}{\partial n_1} & \cdots & n_l\frac{\partial\mu_2}{\partial n_l} - \frac{n_lM_l}{M_1}\frac{\partial\mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\sum_{j=2}^{k} n_jM_j}{M_1}\frac{\partial\mu_l}{\partial n_1} + n_1\frac{\partial\mu_l}{\partial n_1} & n_2\frac{\partial\mu_l}{\partial n_2} - \frac{n_2M_2}{M_1}\frac{\partial\mu_l}{\partial n_1} & \cdots & n_l\frac{\partial\mu_l}{\partial n_l} - \frac{n_lM_l}{M_1}\frac{\partial\mu_l}{\partial n_1} \end{vmatrix}$$

$$= \frac{W^l}{\prod_{j=2}^{l} n_jM_j}\begin{vmatrix} \frac{\sum_{j=1}^{k} n_jM_j}{M_1}\frac{\partial\mu_1}{\partial n_1} & n_2\frac{\partial\mu_1}{\partial n_2} - \frac{n_2M_2}{M_1}\frac{\partial\mu_1}{\partial n_1} & \cdots & n_l\frac{\partial\mu_1}{\partial n_l} - \frac{n_lM_l}{M_1}\frac{\partial\mu_1}{\partial n_1} \\ \frac{\sum_{j=1}^{k} n_jM_j}{M_1}\frac{\partial\mu_2}{\partial n_1} & n_2\frac{\partial\mu_2}{\partial n_2} - \frac{n_2M_2}{M_1}\frac{\partial\mu_2}{\partial n_1} & \cdots & n_l\frac{\partial\mu_2}{\partial n_l} - \frac{n_lM_l}{M_1}\frac{\partial\mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\sum_{j=1}^{k} n_jM_j}{M_1}\frac{\partial\mu_l}{\partial n_1} & n_2\frac{\partial\mu_l}{\partial n_2} - \frac{n_2M_2}{M_1}\frac{\partial\mu_l}{\partial n_1} & \cdots & n_l\frac{\partial\mu_l}{\partial n_l} - \frac{n_lM_l}{M_1}\frac{\partial\mu_l}{\partial n_1} \end{vmatrix}$$

$$= W^l \sum_{j=1}^{k} n_jM_j \begin{vmatrix} \frac{1}{M_1}\frac{\partial\mu_1}{\partial n_1} & \frac{1}{M_2}\frac{\partial\mu_1}{\partial n_2} - \frac{1}{M_1}\frac{\partial\mu_1}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial\mu_1}{\partial n_l} - \frac{1}{M_1}\frac{\partial\mu_1}{\partial n_1} \\ \frac{1}{M_1}\frac{\partial\mu_2}{\partial n_1} & \frac{1}{M_2}\frac{\partial\mu_2}{\partial n_2} - \frac{1}{M_1}\frac{\partial\mu_2}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial\mu_2}{\partial n_l} - \frac{1}{M_1}\frac{\partial\mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{1}{M_1}\frac{\partial\mu_l}{\partial n_1} & \frac{1}{M_2}\frac{\partial\mu_l}{\partial n_2} - \frac{1}{M_1}\frac{\partial\mu_l}{\partial n_1} & \cdots & \frac{1}{M_l}\frac{\partial\mu_l}{\partial n_l} - \frac{1}{M_1}\frac{\partial\mu_l}{\partial n_1} \end{vmatrix}$$

(The first column add to other column)

$$= W^l \sum_{j=1}^{k} n_j M_j \begin{vmatrix} \frac{1}{M_1}\frac{\partial\mu_1}{\partial n_1} & \frac{1}{M_2}\frac{\partial\mu_1}{\partial n_2} & \cdots & \frac{1}{M_l}\frac{\partial\mu_1}{\partial n_l} \\ \frac{1}{M_1}\frac{\partial\mu_2}{\partial n_1} & \frac{1}{M_2}\frac{\partial\mu_2}{\partial n_2} & \cdots & \frac{1}{M_l}\frac{\partial\mu_2}{\partial n_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{1}{M_1}\frac{\partial\mu_l}{\partial n_1} & \frac{1}{M_2}\frac{\partial\mu_l}{\partial n_2} & \cdots & \frac{1}{M_l}\frac{\partial\mu_l}{\partial n_l} \end{vmatrix} = \frac{W^{l+1}}{\prod_{j=1}^{l} M_j} \begin{vmatrix} \frac{\partial\mu_1}{\partial n_1} & \frac{\partial\mu_1}{\partial n_2} & \cdots & \frac{\partial\mu_1}{\partial n_l} \\ \frac{\partial\mu_2}{\partial n_1} & \frac{\partial\mu_2}{\partial n_2} & \cdots & \frac{\partial\mu_2}{\partial n_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial n_1} & \frac{\partial\mu_l}{\partial n_2} & \cdots & \frac{\partial\mu_l}{\partial n_l} \end{vmatrix}$$

viz.

$$\sum_{j=l+1}^{k} w_j \begin{vmatrix} \frac{\partial\mu_1}{\partial w_1} & \frac{\partial\mu_1}{\partial w_2} & \cdots & \frac{\partial\mu_1}{\partial w_l} \\ \frac{\partial\mu_2}{\partial w_1} & \frac{\partial\mu_2}{\partial w_2} & \cdots & \frac{\partial\mu_2}{\partial w_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial w_1} & \frac{\partial\mu_l}{\partial w_2} & \cdots & \frac{\partial\mu_l}{\partial w_l} \end{vmatrix}_j = \frac{W^l}{\prod_{j=1}^{l} M_j} \begin{vmatrix} \frac{\partial\mu_1}{\partial n_1} & \frac{\partial\mu_1}{\partial n_2} & \cdots & \frac{\partial\mu_1}{\partial n_l} \\ \frac{\partial\mu_2}{\partial n_1} & \frac{\partial\mu_2}{\partial n_2} & \cdots & \frac{\partial\mu_2}{\partial n_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial n_1} & \frac{\partial\mu_l}{\partial n_2} & \cdots & \frac{\partial\mu_l}{\partial n_l} \end{vmatrix} \quad (l = 1, 2, \ldots, k-1). \tag{46}$$

By equation (25) and equation (46) we obtain

$$\sum_{j=l+1}^{k} w_j \begin{vmatrix} \frac{\partial\mu_1}{\partial w_1} & \frac{\partial\mu_1}{\partial w_2} & \cdots & \frac{\partial\mu_1}{\partial w_l} \\ \frac{\partial\mu_2}{\partial w_1} & \frac{\partial\mu_2}{\partial w_2} & \cdots & \frac{\partial\mu_2}{\partial w_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial w_1} & \frac{\partial\mu_l}{\partial w_2} & \cdots & \frac{\partial\mu_l}{\partial w_l} \end{vmatrix}_j > 0. \quad (l = 1, 2, \ldots, k-1). \tag{47}$$

Equation (47) is just the stability condition of phase equilibrium for concentration variables w_i. The left of equation (47) is the sum of $(k-l)$ different determinants with l order. We only able to confirm the sign of the determinant with $(k-1)$ order, because when $l = k-1$, equation (47) becomes

$$\begin{vmatrix} \frac{\partial\mu_1}{\partial w_1} & \frac{\partial\mu_1}{\partial w_2} & \cdots & \frac{\partial\mu_1}{\partial w_{k-1}} \\ \frac{\partial\mu_2}{\partial w_1} & \frac{\partial\mu_2}{\partial w_2} & \cdots & \frac{\partial\mu_2}{\partial w_{k-1}} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_{k-1}}{\partial w_1} & \frac{\partial\mu_{k-1}}{\partial w_2} & \cdots & \frac{\partial\mu_{k-1}}{\partial w_{k-1}} \end{vmatrix} > 0. \tag{48}$$

2.6. *The stability condition of phase equilibrium for concentration variables c_i*

Due to molarity $c_i = n_i/V$ (V is the total volume of the system), so

$$\begin{aligned} \mathrm{d}\mu_i &= \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}n_j = \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}\left(Vc_j\right) \\ &= \sum_{j=1}^{k} c_j \frac{\partial \mu_i}{\partial n_j} \mathrm{d}V + V \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}c_j \\ &= \sum_{j=1}^{k} n_j \frac{\partial \mu_i}{\partial n_j} \frac{\mathrm{d}V}{V} + V \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}c_j \\ &= V \sum_{j=1}^{k} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}c_j = V \sum_{j=1}^{k-1} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}c_j + V \frac{\partial \mu_i}{\partial n_k} \mathrm{d}c_k. \end{aligned} \tag{49}$$

Due to

$$V = \sum_{i=1}^{k} n_i \overline{V}_i = \sum_{i=1}^{k} V c_i \overline{V}_i \quad \text{viz.} \quad 1 = \sum_{i=1}^{k} c_i \overline{V}_i, \tag{50}$$

where $\overline{V}_i = (\partial V/\partial n_i)_{T,p,n_j}$ is partial mole volume of component i. Differentiating equation (50), we obtain

$$0 = \sum_{i=1}^{k} c_i \mathrm{d}\overline{V}_i + \sum_{i=1}^{k} \overline{V}_i \mathrm{d}c_i = \sum_{i=1}^{k} \overline{V}_i \mathrm{d}c_i \tag{51}$$

or

$$\mathrm{d}c_k = -\frac{1}{\overline{V}_k} \sum_{j=1}^{k-1} \overline{V}_j \mathrm{d}c_j. \tag{52}$$

Equation (52) is just the restrictive condition of molarity c_j. Substituting equation (52) into (49), we obtain

$$\mathrm{d}\mu_i = V \sum_{j=1}^{k-1} \frac{\partial \mu_i}{\partial n_j} \mathrm{d}c_j - \frac{\partial \mu_i}{\partial n_k} \frac{V}{\overline{V}_k} \sum_{j=1}^{k-1} \overline{V}_j \mathrm{d}c_j = V \sum_{j=1}^{k-1} \left(\frac{\partial \mu_i}{\partial n_j} - \frac{\partial \mu_i}{\partial n_k} \frac{\overline{V}_j}{\overline{V}_k} \right) \mathrm{d}c_j. \tag{53}$$

By equation (53) we obtain

$$\frac{\partial \mu_i}{\partial c_j} = V \left(\frac{\partial \mu_i}{\partial n_j} - \frac{\overline{V}_j}{\overline{V}_k} \frac{\partial \mu_i}{\partial n_k} \right) \quad (j = 1, 2, \ldots, k-1). \tag{54}$$

By equation (54) we obtain

$$
\begin{vmatrix}
\frac{\partial \mu_1}{\partial c_1} & \frac{\partial \mu_1}{\partial c_2} & \cdots & \frac{\partial \mu_1}{\partial c_l} \\
\frac{\partial \mu_2}{\partial c_1} & \frac{\partial \mu_2}{\partial c_2} & \cdots & \frac{\partial \mu_2}{\partial c_l} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{\partial \mu_l}{\partial c_1} & \frac{\partial \mu_l}{\partial c_2} & \cdots & \frac{\partial \mu_l}{\partial c_l}
\end{vmatrix}
$$

$$
= V^l \begin{vmatrix}
\frac{\partial \mu_1}{\partial n_1} - \frac{\overline{V}_1}{\overline{V}_k}\frac{\partial \mu_1}{\partial n_k} & \frac{\partial \mu_1}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_k}\frac{\partial \mu_1}{\partial n_k} & \cdots & \frac{\partial \mu_1}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_k}\frac{\partial \mu_1}{\partial n_k} \\
\frac{\partial \mu_2}{\partial n_1} - \frac{\overline{V}_1}{\overline{V}_k}\frac{\partial \mu_2}{\partial n_k} & \frac{\partial \mu_2}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_k}\frac{\partial \mu_2}{\partial n_k} & \cdots & \frac{\partial \mu_2}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_k}\frac{\partial \mu_2}{\partial n_k} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{\partial \mu_l}{\partial n_1} - \frac{\overline{V}_1}{\overline{V}_k}\frac{\partial \mu_l}{\partial n_k} & \frac{\partial \mu_l}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_k}\frac{\partial \mu_l}{\partial n_k} & \cdots & \frac{\partial \mu_l}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_k}\frac{\partial \mu_l}{\partial n_k}
\end{vmatrix}
$$

$$
= V^l \prod_{j=1}^{l} \overline{V}_j \begin{vmatrix}
\frac{1}{\overline{V}_1}\frac{\partial \mu_1}{\partial n_1} - \frac{1}{\overline{V}_k}\frac{\partial \mu_1}{\partial n_k} & \frac{1}{\overline{V}_2}\frac{\partial \mu_1}{\partial n_2} - \frac{1}{\overline{V}_k}\frac{\partial \mu_1}{\partial n_k} & \cdots & \frac{1}{\overline{V}_l}\frac{\partial \mu_1}{\partial n_l} - \frac{1}{\overline{V}_k}\frac{\partial \mu_1}{\partial n_k} \\
\frac{1}{\overline{V}_1}\frac{\partial \mu_2}{\partial n_1} - \frac{1}{\overline{V}_k}\frac{\partial \mu_2}{\partial n_k} & \frac{1}{\overline{V}_2}\frac{\partial \mu_2}{\partial n_2} - \frac{1}{\overline{V}_k}\frac{\partial \mu_2}{\partial n_k} & \cdots & \frac{1}{\overline{V}_l}\frac{\partial \mu_2}{\partial n_l} - \frac{1}{\overline{V}_k}\frac{\partial \mu_2}{\partial n_k} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{1}{\overline{V}_1}\frac{\partial \mu_l}{\partial n_1} - \frac{1}{\overline{V}_k}\frac{\partial \mu_l}{\partial n_k} & \frac{1}{\overline{V}_2}\frac{\partial \mu_l}{\partial n_2} - \frac{1}{\overline{V}_k}\frac{\partial \mu_l}{\partial n_k} & \cdots & \frac{1}{\overline{V}_l}\frac{\partial \mu_l}{\partial n_l} - \frac{1}{\overline{V}_k}\frac{\partial \mu_l}{\partial n_k}
\end{vmatrix}
$$

(The first column multiplied by negative sign add to other column)

$$
= V^l \prod_{j=1}^{l} \overline{V}_j \begin{vmatrix}
\frac{1}{\overline{V}_1}\frac{\partial \mu_1}{\partial n_1} - \frac{1}{\overline{V}_k}\frac{\partial \mu_1}{\partial n_k} & \frac{1}{\overline{V}_2}\frac{\partial \mu_1}{\partial n_2} - \frac{1}{\overline{V}_1}\frac{\partial \mu_1}{\partial n_1} & \cdots & \frac{1}{\overline{V}_l}\frac{\partial \mu_1}{\partial n_l} - \frac{1}{\overline{V}_1}\frac{\partial \mu_1}{\partial n_1} \\
\frac{1}{\overline{V}_1}\frac{\partial \mu_2}{\partial n_1} - \frac{1}{\overline{V}_k}\frac{\partial \mu_2}{\partial n_k} & \frac{1}{\overline{V}_2}\frac{\partial \mu_2}{\partial n_2} - \frac{1}{\overline{V}_1}\frac{\partial \mu_2}{\partial n_1} & \cdots & \frac{1}{\overline{V}_l}\frac{\partial \mu_2}{\partial n_l} - \frac{1}{\overline{V}_1}\frac{\partial \mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{1}{\overline{V}_1}\frac{\partial \mu_l}{\partial n_1} - \frac{1}{\overline{V}_k}\frac{\partial \mu_l}{\partial n_k} & \frac{1}{\overline{V}_2}\frac{\partial \mu_l}{\partial n_2} - \frac{1}{\overline{V}_1}\frac{\partial \mu_l}{\partial n_1} & \cdots & \frac{1}{\overline{V}_l}\frac{\partial \mu_l}{\partial n_l} - \frac{1}{\overline{V}_1}\frac{\partial \mu_l}{\partial n_1}
\end{vmatrix}
$$

$$
= V^l \begin{vmatrix}
\frac{\partial \mu_1}{\partial n_1} - \frac{\overline{V}_1}{\overline{V}_k}\frac{\partial \mu_1}{\partial n_k} & \frac{\partial \mu_1}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial \mu_1}{\partial n_1} & \cdots & \frac{\partial \mu_1}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial \mu_1}{\partial n_1} \\
\frac{\partial \mu_2}{\partial n_1} - \frac{\overline{V}_1}{\overline{V}_k}\frac{\partial \mu_2}{\partial n_k} & \frac{\partial \mu_2}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial \mu_2}{\partial n_1} & \cdots & \frac{\partial \mu_2}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial \mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{\partial \mu_l}{\partial n_1} - \frac{\overline{V}_1}{\overline{V}_k}\frac{\partial \mu_l}{\partial n_k} & \frac{\partial \mu_l}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial \mu_l}{\partial n_1} & \cdots & \frac{\partial \mu_l}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial \mu_l}{\partial n_1}
\end{vmatrix} \tag{55}
$$

Every component from $(l+1)$ to k may be regarded as component k. So we change subscript k in determinant on the right of equation (55) into j, add subscript j to determinant on the left equation (55), multiply two side of equation (55) by $n_j\overline{V}_j$, and then find sum from $(l+1)$ to k:

$$\sum_{j=l+1}^{k} n_j\overline{V}_j \begin{vmatrix} \frac{\partial\mu_1}{\partial c_1} & \frac{\partial\mu_1}{\partial c_2} & \cdots & \frac{\partial\mu_1}{\partial c_l} \\ \frac{\partial\mu_2}{\partial c_1} & \frac{\partial\mu_2}{\partial c_2} & \cdots & \frac{\partial\mu_2}{\partial c_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial c_1} & \frac{\partial\mu_l}{\partial c_2} & \cdots & \frac{\partial\mu_l}{\partial c_l} \end{vmatrix}_j$$

$$= V^l \sum_{j=l+1}^{k} n_j\overline{V}_j \begin{vmatrix} \frac{\partial\mu_1}{\partial n_1} - \frac{\overline{V}_1}{\overline{V}_j}\frac{\partial\mu_1}{\partial n_j} & \frac{\partial\mu_1}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial\mu_1}{\partial n_1} & \cdots & \frac{\partial\mu_1}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial\mu_1}{\partial n_1} \\ \frac{\partial\mu_2}{\partial n_1} - \frac{\overline{V}_1}{\overline{V}_j}\frac{\partial\mu_2}{\partial n_j} & \frac{\partial\mu_2}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial\mu_2}{\partial n_1} & \cdots & \frac{\partial\mu_2}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial\mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial n_1} - \frac{\overline{V}_1}{\overline{V}_j}\frac{\partial\mu_l}{\partial n_j} & \frac{\partial\mu_l}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial\mu_l}{\partial n_1} & \cdots & \frac{\partial\mu_l}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial\mu_l}{\partial n_1} \end{vmatrix}$$

$$= V^l \begin{vmatrix} \sum_{j=l+1}^{k} n_j\overline{V}_j\frac{\partial\mu_1}{\partial n_1} - \overline{V}_1\sum_{j=l+1}^{k} n_j\frac{\partial\mu_1}{\partial n_j} & \frac{\partial\mu_1}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial\mu_1}{\partial n_1} & \cdots & \frac{\partial\mu_1}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial\mu_1}{\partial n_1} \\ \sum_{j=l+1}^{k} n_j\overline{V}_j\frac{\partial\mu_2}{\partial n_1} - \overline{V}_1\sum_{j=l+1}^{k} n_j\frac{\partial\mu_2}{\partial n_j} & \frac{\partial\mu_2}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial\mu_2}{\partial n_1} & \cdots & \frac{\partial\mu_2}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial\mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \sum_{j=l+1}^{k} n_j\overline{V}_j\frac{\partial\mu_l}{\partial n_1} - \overline{V}_1\sum_{j=l+1}^{k} n_j\frac{\partial\mu_l}{\partial n_j} & \frac{\partial\mu_l}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial\mu_l}{\partial n_1} & \cdots & \frac{\partial\mu_l}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial\mu_l}{\partial n_1} \end{vmatrix}$$

$$= V^l \begin{vmatrix} \sum_{j=l+1}^{k} n_j\overline{V}_j\frac{\partial\mu_1}{\partial n_1} + \overline{V}_1\sum_{j=1}^{l} n_j\frac{\partial\mu_1}{\partial n_j} & \frac{\partial\mu_1}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial\mu_1}{\partial n_1} & \cdots & \frac{\partial\mu_1}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial\mu_1}{\partial n_1} \\ \sum_{j=l+1}^{k} n_j\overline{V}_j\frac{\partial\mu_2}{\partial n_1} + \overline{V}_1\sum_{j=1}^{l} n_j\frac{\partial\mu_2}{\partial n_j} & \frac{\partial\mu_2}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial\mu_2}{\partial n_1} & \cdots & \frac{\partial\mu_2}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial\mu_2}{\partial n_1} \\ \cdots & \cdots & \cdots & \cdots \\ \sum_{j=l+1}^{k} n_j\overline{V}_j\frac{\partial\mu_l}{\partial n_1} + \overline{V}_1\sum_{j=1}^{l} n_j\frac{\partial\mu_l}{\partial n_j} & \frac{\partial\mu_l}{\partial n_2} - \frac{\overline{V}_2}{\overline{V}_1}\frac{\partial\mu_l}{\partial n_1} & \cdots & \frac{\partial\mu_l}{\partial n_l} - \frac{\overline{V}_l}{\overline{V}_1}\frac{\partial\mu_l}{\partial n_1} \end{vmatrix}$$

(Multiply column 2 by $n_2\overline{V}_1$, multiply column 3 by $n_3\overline{V}_1$, … multiply column l by $n_l\overline{V}_1$)

$$
= \frac{V^l}{(\overline{V}_1)^{l-1}\prod_{j=2}^{l} n_j}
\begin{vmatrix}
\sum_{j=l+1}^{k} n_j\overline{V}_j\frac{\partial\mu_1}{\partial n_1} + \overline{V}_1\sum_{j=1}^{l} n_j\frac{\partial\mu_1}{\partial n_j} & n_2\overline{V}_1\frac{\partial\mu_1}{\partial n_2} - n_2\overline{V}_2\frac{\partial\mu_1}{\partial n_1} & \cdots & n_l\overline{V}_1\frac{\partial\mu_1}{\partial n_l} - n_l\overline{V}_l\frac{\partial\mu_1}{\partial n_1} \\
\sum_{j=l+1}^{k} n_j\overline{V}_j\frac{\partial\mu_2}{\partial n_1} + \overline{V}_1\sum_{j=1}^{l} n_j\frac{\partial\mu_2}{\partial n_j} & n_2\overline{V}_1\frac{\partial\mu_2}{\partial n_2} - n_2\overline{V}_2\frac{\partial\mu_2}{\partial n_1} & \cdots & n_l\overline{V}_1\frac{\partial\mu_2}{\partial n_l} - n_l\overline{V}_l\frac{\partial\mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\sum_{j=l+1}^{k} n_j\overline{V}_j\frac{\partial\mu_l}{\partial n_1} + \overline{V}_1\sum_{j=1}^{l} n_j\frac{\partial\mu_l}{\partial n_j} & n_2\overline{V}_1\frac{\partial\mu_l}{\partial n_2} - n_2\overline{V}_2\frac{\partial\mu_l}{\partial n_1} & \cdots & n_l\overline{V}_1\frac{\partial\mu_l}{\partial n_l} - n_l\overline{V}_l\frac{\partial\mu_l}{\partial n_1}
\end{vmatrix}
$$

(Every column multiplied by negative sign add to the first column)

$$
= \frac{V^l}{(\overline{V}_1)^{l-1}\prod_{j=2}^{l} n_j}
\begin{vmatrix}
\sum_{j=2}^{k} n_j\overline{V}_j\frac{\partial\mu_1}{\partial n_1} + \overline{V}_1 n_1\frac{\partial\mu_1}{\partial n_1} & n_2\overline{V}_1\frac{\partial\mu_1}{\partial n_2} - n_2\overline{V}_2\frac{\partial\mu_1}{\partial n_1} & \cdots & n_l\overline{V}_1\frac{\partial\mu_1}{\partial n_l} - n_l\overline{V}_l\frac{\partial\mu_1}{\partial n_1} \\
\sum_{j=2}^{k} n_j\overline{V}_j\frac{\partial\mu_2}{\partial n_1} + \overline{V}_1 n_1\frac{\partial\mu_2}{\partial n_1} & n_2\overline{V}_1\frac{\partial\mu_2}{\partial n_2} - n_2\overline{V}_2\frac{\partial\mu_2}{\partial n_1} & \cdots & n_l\overline{V}_1\frac{\partial\mu_2}{\partial n_l} - n_l\overline{V}_l\frac{\partial\mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\sum_{j=2}^{k} n_j\overline{V}_j\frac{\partial\mu_l}{\partial n_1} + \overline{V}_1 n_1\frac{\partial\mu_l}{\partial n_1} & n_2\overline{V}_1\frac{\partial\mu_l}{\partial n_2} - n_2\overline{V}_2\frac{\partial\mu_l}{\partial n_1} & \cdots & n_l\overline{V}_1\frac{\partial\mu_l}{\partial n_l} - n_l\overline{V}_l\frac{\partial\mu_l}{\partial n_1}
\end{vmatrix}
$$

$$
= \frac{V^l}{(\overline{V}_1)^{l-1}\prod_{j=2}^{l} n_j}
\begin{vmatrix}
\sum_{j=1}^{k} n_j\overline{V}_j\frac{\partial\mu_1}{\partial n_1} & n_2\overline{V}_1\frac{\partial\mu_1}{\partial n_2} - n_2\overline{V}_2\frac{\partial\mu_1}{\partial n_1} & \cdots & n_l\overline{V}_1\frac{\partial\mu_1}{\partial n_l} - n_l\overline{V}_l\frac{\partial\mu_1}{\partial n_1} \\
\sum_{j=1}^{k} n_j\overline{V}_j\frac{\partial\mu_2}{\partial n_1} & n_2\overline{V}_1\frac{\partial\mu_2}{\partial n_2} - n_2\overline{V}_2\frac{\partial\mu_2}{\partial n_1} & \cdots & n_l\overline{V}_1\frac{\partial\mu_2}{\partial n_l} - n_l\overline{V}_l\frac{\partial\mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\sum_{j=1}^{k} n_j\overline{V}_j\frac{\partial\mu_l}{\partial n_1} & n_2\overline{V}_1\frac{\partial\mu_l}{\partial n_2} - n_2\overline{V}_2\frac{\partial\mu_l}{\partial n_1} & \cdots & n_l\overline{V}_1\frac{\partial\mu_l}{\partial n_l} - n_l\overline{V}_l\frac{\partial\mu_l}{\partial n_1}
\end{vmatrix}
$$

$$
= \frac{V^{l+1}}{(\overline{V}_1)^{l-1}}
\begin{vmatrix}
\frac{\partial\mu_1}{\partial n_1} & \overline{V}_1\frac{\partial\mu_1}{\partial n_2} - \overline{V}_2\frac{\partial\mu_1}{\partial n_1} & \cdots & \overline{V}_1\frac{\partial\mu_1}{\partial n_l} - \overline{V}_l\frac{\partial\mu_1}{\partial n_1} \\
\frac{\partial\mu_2}{\partial n_1} & \overline{V}_1\frac{\partial\mu_2}{\partial n_2} - \overline{V}_2\frac{\partial\mu_2}{\partial n_1} & \cdots & \overline{V}_1\frac{\partial\mu_2}{\partial n_l} - \overline{V}_l\frac{\partial\mu_2}{\partial n_1} \\
\cdots & \cdots & \cdots & \cdots \\
\frac{\partial\mu_l}{\partial n_1} & \overline{V}_1\frac{\partial\mu_l}{\partial n_2} - \overline{V}_2\frac{\partial\mu_l}{\partial n_1} & \cdots & \overline{V}_1\frac{\partial\mu_l}{\partial n_l} - \overline{V}_l\frac{\partial\mu_l}{\partial n_1}
\end{vmatrix}
$$

(Column 1 multiplied by $\overline{V}_2$ add to column 2, column 1 multiplied by $\overline{V}_3$ add to column 3, ... column 1 multiplied by $\overline{V}_l$ add to column l)

$$= \frac{V^{l+1}}{(\overline{V}_1)^{l-1}} \begin{vmatrix} \frac{\partial \mu_1}{\partial n_1} & \overline{V}_1 \frac{\partial \mu_1}{\partial n_2} & \cdots & \overline{V}_1 \frac{\partial \mu_1}{\partial n_l} \\ \frac{\partial \mu_2}{\partial n_1} & \overline{V}_1 \frac{\partial \mu_2}{\partial n_2} & \cdots & \overline{V}_1 \frac{\partial \mu_2}{\partial n_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial n_1} & \overline{V}_1 \frac{\partial \mu_l}{\partial n_2} & \cdots & \overline{V}_1 \frac{\partial \mu_l}{\partial n_l} \end{vmatrix} = V^{l+1} \begin{vmatrix} \frac{\partial \mu_1}{\partial n_1} & \frac{\partial \mu_1}{\partial n_2} & \cdots & \frac{\partial \mu_1}{\partial n_l} \\ \frac{\partial \mu_2}{\partial n_1} & \frac{\partial \mu_2}{\partial n_2} & \cdots & \frac{\partial \mu_2}{\partial n_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial n_1} & \frac{\partial \mu_l}{\partial n_2} & \cdots & \frac{\partial \mu_l}{\partial n_l} \end{vmatrix} \tag{56}$$

V divide into equation (56):

$$\sum_{j=l+1}^{k} c_j \overline{V}_j \begin{vmatrix} \frac{\partial \mu_1}{\partial c_1} & \frac{\partial \mu_1}{\partial c_2} & \cdots & \frac{\partial \mu_1}{\partial c_l} \\ \frac{\partial \mu_2}{\partial c_1} & \frac{\partial \mu_2}{\partial c_2} & \cdots & \frac{\partial \mu_2}{\partial c_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial c_1} & \frac{\partial \mu_l}{\partial c_2} & \cdots & \frac{\partial \mu_l}{\partial c_l} \end{vmatrix}_j = V^l \begin{vmatrix} \frac{\partial \mu_1}{\partial n_1} & \frac{\partial \mu_1}{\partial n_2} & \cdots & \frac{\partial \mu_1}{\partial n_l} \\ \frac{\partial \mu_2}{\partial n_1} & \frac{\partial \mu_2}{\partial n_2} & \cdots & \frac{\partial \mu_2}{\partial n_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial n_1} & \frac{\partial \mu_l}{\partial n_2} & \cdots & \frac{\partial \mu_l}{\partial n_l} \end{vmatrix} \quad (l = 1, 2, \ldots, k-1). \tag{57}$$

By equation (25) and (57) we obtain

$$\sum_{j=l+1}^{k} c_j \overline{V}_j \begin{vmatrix} \frac{\partial \mu_1}{\partial c_1} & \frac{\partial \mu_1}{\partial c_2} & \cdots & \frac{\partial \mu_1}{\partial c_l} \\ \frac{\partial \mu_2}{\partial c_1} & \frac{\partial \mu_2}{\partial c_2} & \cdots & \frac{\partial \mu_2}{\partial c_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_l}{\partial c_1} & \frac{\partial \mu_l}{\partial c_2} & \cdots & \frac{\partial \mu_l}{\partial c_l} \end{vmatrix}_j > 0 \quad (l = 1, 2, \ldots, k-1). \tag{58}$$

Equation (58) is just the stability condition of phase equilibrium for concentration variables c_i. The left of equation (58) is the sum of $(k-l)$ different determinant with l order. When $l = k-1$, equation (58) becomes

$$c_k \overline{V}_k \begin{vmatrix} \frac{\partial \mu_1}{\partial c_1} & \frac{\partial \mu_1}{\partial c_2} & \cdots & \frac{\partial \mu_1}{\partial c_{k-1}} \\ \frac{\partial \mu_2}{\partial c_1} & \frac{\partial \mu_2}{\partial c_2} & \cdots & \frac{\partial \mu_2}{\partial c_{k-1}} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_{k-1}}{\partial c_1} & \frac{\partial \mu_{k-1}}{\partial c_2} & \cdots & \frac{\partial \mu_{k-1}}{\partial c_{k-1}} \end{vmatrix} > 0 \tag{59}$$

c_i is always positive, but $\overline{V}_i$ may be either positive or negative. For example, $\overline{V}_{MgSO_4}$ of $MgSO_4$ in aquatic solution is negative [6]. Hence, if $\overline{V}_k$ is positive, equation (59) becomes

$$\begin{vmatrix} \frac{\partial\mu_1}{\partial c_1} & \frac{\partial\mu_1}{\partial c_2} & \cdots & \frac{\partial\mu_1}{\partial c_{k-1}} \\ \frac{\partial\mu_2}{\partial c_1} & \frac{\partial\mu_2}{\partial c_2} & \cdots & \frac{\partial\mu_2}{\partial c_{k-1}} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_{k-1}}{\partial c_1} & \frac{\partial\mu_{k-1}}{\partial c_2} & \cdots & \frac{\partial\mu_{k-1}}{\partial c_{k-1}} \end{vmatrix} > 0 \quad (\overline{V}_k > 0). \tag{60}$$

Otherwise

$$\begin{vmatrix} \frac{\partial\mu_1}{\partial c_1} & \frac{\partial\mu_1}{\partial c_2} & \cdots & \frac{\partial\mu_1}{\partial c_{k-1}} \\ \frac{\partial\mu_2}{\partial c_1} & \frac{\partial\mu_2}{\partial c_2} & \cdots & \frac{\partial\mu_2}{\partial c_{k-1}} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_{k-1}}{\partial c_1} & \frac{\partial\mu_{k-1}}{\partial c_2} & \cdots & \frac{\partial\mu_{k-1}}{\partial c_{k-1}} \end{vmatrix} < 0 \quad (\overline{V}_k < 0). \tag{61}$$

Chemical potential of ideal gases only depends on molarity c_i. So for ideal gases, determinant on the left of equation (58) is independent of c_j, and $\overline{V}_j = RT/p$. Thus for ideal gases, equation (58) becomes

$$\begin{vmatrix} \frac{\partial\mu_1}{\partial c_1} & \frac{\partial\mu_1}{\partial c_2} & \cdots & \frac{\partial\mu_1}{\partial c_l} \\ \frac{\partial\mu_2}{\partial c_1} & \frac{\partial\mu_2}{\partial c_2} & \cdots & \frac{\partial\mu_2}{\partial c_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial c_1} & \frac{\partial\mu_l}{\partial c_2} & \cdots & \frac{\partial\mu_l}{\partial c_l} \end{vmatrix} \sum_{j=l+1}^{k} c_j > 0 \quad \text{or} \quad \begin{vmatrix} \frac{\partial\mu_1}{\partial c_1} & \frac{\partial\mu_1}{\partial c_2} & \cdots & \frac{\partial\mu_1}{\partial c_l} \\ \frac{\partial\mu_2}{\partial c_1} & \frac{\partial\mu_2}{\partial c_2} & \cdots & \frac{\partial\mu_2}{\partial c_l} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial\mu_l}{\partial c_1} & \frac{\partial\mu_l}{\partial c_2} & \cdots & \frac{\partial\mu_l}{\partial c_l} \end{vmatrix} > 0 \quad (l = 1, 2, \ldots, k-1) \tag{62}$$

or

$$\begin{vmatrix} \frac{RT}{c_1} & 0 & \cdots & 0 \\ 0 & \frac{RT}{c_2} & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \frac{RT}{c_l} \end{vmatrix} = \frac{(RT)^l}{\prod_{i=1}^{l} c_i} > 0. \tag{63}$$

3. Conclusion

The stability conditions of phase equilibrium for various concentration variables are educed according to thermodynamic principle. When a system with k components arrives at stable equilibrium, if the mole number n_i or the mole fraction $y_i(= n_i/n_k)$ or molality $m_i[= n_i/(n_k M_k)]$ of component i $(i = 1, 2 \cdots k-1)$ are elected as concentration variables, thermodynamic theory is able to confirm that the sign of every order determinant composed of the second-order partial differential of chemical potential with respect to these concentration variables is positive; if the mole fraction $x_i(= n_i/n)$ or mass fraction $w_i(= n_i M_i/W)$ are elected as the concentration variables, thermodynamic theory is only able to confirm that the sign of $(k-1)$ order determinant is positive; if molarity $c_i(= n_i/V)$ are elected as the concentration variables, thermodynamic theory is not able to confirm the sign of every order determinant

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