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多元复相平衡体系热力学变量的微分关系

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摘 要： 根据相平衡原理，导出了无绝热壁、刚性壁和半透壁及无化学反应、除相平衡条件约束外无其他约束的 k 组分和 φ 相（$2\leqslant\varphi\leqslant k-1$）的多元复相平衡体系非独立变量与独立变量之间的微分关系. 任一相有温度、压力和（$k-1$）个摩尔分数共（$k+1$）个变量，其中温度和压力是各相的公共变量；k 组分复相平衡体系的独立变量个数最多为 k，把温度和压力作为首选的独立变量，独立的浓度变量最多为（$k-2$）把独立的浓度变量全部选在第一相，而把其他相的浓度变量都做非独立变量，第一相至少有一个非独立的浓度变量.

关键词： 多元系；相平衡；自由度；相律
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The Differential Relationships of Thermodynamic Variables for the Equilibrium of Heterogeneous Substances

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Abstract For the system without adiabatic walls, rigid walls or semi-permeable walls and without chemical reactions or without other restrictions except restrictions of phase equilibrium conditions, if the number of components of the system is k and the number of phases is φ, the degree of freedom of the system at equilibrium is $f=k-\varphi+2$. Because the degree of freedom is incapable of being negative, $f=k-\varphi+2\geqslant 0$, viz. $\varphi\leqslant k+2$. For the heterogeneous equilibrium, the number of phases is at least 2, so $\varphi=k+2-f\geqslant 2$, viz. $f\leqslant k$. Hence the range of change of φ and f is $2\leqslant\varphi\leqslant k+2$, $0\leqslant f\leqslant k$, respectitvely. If $\varphi=k+2$, there are no independent variables in the system at equilibrium. If $\varphi=k+1$, there is one independent variable; if the temperature is selected as the independent variable, the other dependent variables can be expressed as the function of the temperature. If $\varphi=k$, there are two independent variables; if the temperature and pressure are selected as the independent variables, the other dependent variables can be expressed as the function of the temperature and pressure. If $2\leqslant\varphi\leqslant k-1$, there are more than two independent variables; if the temperature, pressure and some concentrations are selected as independent variables, the other dependent variables can be expressed as the function of the temperature, pressure and these concentrations. The differential relationships of dependent variables and independent variables are educed out according to the principle of phase equilibriums for $2\leqslant\varphi\leqslant k-1$. In any phase the number of the variables is $(k+1)$, viz. temperature T, pressure p and $(k-1)$ mole fractions $x_1, x_2, \cdots, x_{k-1}$. The temperature and pressure are common variables of every phase. The number of independent variables is at best k for the heterogeneous equilibriums of k components. The temperature, pressure and $(k-2)$ concentrations are selected as independent variables. The independent concentration variables are selected entirely from the first phase and the concentration variables of the other

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phases all act as dependent variables. There is at least one dependent concentration variable in the first phase.
Keywords　Systems of heterogeneous substances, Phase equilibrium, Degree of freedom, Phase rule

1　引　言

对于无绝热壁、刚性壁和半透壁及无化学反应、除相平衡条件约束外无其他约束的体系，如果体系的组分数是 k，相数为 φ，则平衡时体系的自由度为 $f=k-\varphi+2$. 由于自由度不能为负，即 $f=k-\varphi+2\geqslant 0$，所以 $\varphi\leqslant k+2$. 又对复相体系，相数最少应为 2，即 $\varphi=k+2-f\geqslant 2$，所以，$f\leqslant k$. 因此，多元复相平衡体系 φ 和 f 的变化范围为 $2\leqslant\varphi\leqslant k+2$，$0\leqslant f\leqslant k$. 如果 $\varphi=k+2$，则平衡时体系无独立变量. 如果 $\varphi=k+1$，则平衡时体系有一个独立变量 如果选择温度做独立变量，则其他非独立变量都可表示为温度的函数[1]. 如果 $\varphi=k$，则平衡时体系有两个独立变量 如果选择温度和压力做独立变量，则其他非独立变量都可表示为温度和压力的函数[2]. 如果 $2\leqslant\varphi\leqslant k-1$，则平衡时体系有两个以上的独立变量 如果选择温度、压力和一些浓度做独立变量，则其他非独立变量都可表示为温度、压力和这些浓度的函数. 我们就在 $2\leqslant\varphi\leqslant k-1$ 的情形下体系非独立变量与独立变量之间的微分关系进行讨论.

2　第一相非独立变量和独立变量之间的微分关系

我们知道，任一相的变量个数为 $(k+1)$，即温度 (T)、压力 (p) 和 $(k-1)$ 摩尔分数 $(x_1, x_2, \cdots, x_{k-1})$，其中温度和压力是各相的公共变量. 如前所述，$k$ 组分复相平衡体系的独立变量个数最多为 k，如果把温度和压力作为首选的独立变量，则独立的浓度变量最多为 $(k-2)$. 因此，可把独立的浓度变量全部选在某一相，而把其他相的浓度变量都做非独立变量. 现在把独立的浓度变量全部选在第一相. 显然，第一相至少有一个非独立的浓度变量. 我们先导出第一相非独立的浓度变量和独立变量之间的微分关系. 由欧拉齐次函数定律可以证明[3]，均相体系的强度量一般是温度 (T)、压力 (p) 和 $(k-1)$ 摩尔分数 $(x_1, x_2, \cdots, x_{k-1})$ 的函数. 因此，化学势 μ_i 的微分为

$$\mathrm{d}\mu_i = -\bar{S}_i\mathrm{d}T + \bar{V}_i\mathrm{d}p + \sum_{j=1}^{k-1}\frac{\partial\mu_i}{\partial x_j}\mathrm{d}x_j \quad (i=1,2,\cdots,k) \tag{1}$$

或

$$\sum_{j=1}^{k-1}\frac{\partial\mu_i}{\partial x_j}\mathrm{d}x_j = \mathrm{d}\mu_i + \bar{S}_i\mathrm{d}T - \bar{V}_i\mathrm{d}p \quad (i=1,2,\cdots,k) \tag{2}$$

式(2)中 k 个等式不是独立的，因为将第 $1,2,\cdots,k$ 个等式依次乘 $(x_1, x_2, \cdots, x_k)$，然后相加，得"$0=0$"，证明如下：将式(2)两边乘 x_i，然后求和，得

$$\sum_{j=1}^{k-1}\sum_{i=1}^{k}x_i\frac{\partial\mu_i}{\partial x_j}\mathrm{d}x_j = \sum_{i=1}^{k}x_i\mathrm{d}\mu_i + \sum_{i=1}^{k}x_i\bar{S}_i\mathrm{d}T - \sum_{i=1}^{k}x_i\bar{V}_i\mathrm{d}p = \sum_{i=1}^{k}x_i\mathrm{d}\mu_i + S_m\mathrm{d}T - V_m\mathrm{d}p$$

将 $\sum_{i=1}^{k}x_i\frac{\partial\mu_i}{\partial x_j}=0$，$\sum_{i=1}^{k}x_i\mathrm{d}\mu_i = -S_m\mathrm{d}T + V_m\mathrm{d}p$ 代入上式，得

$$0 = -S_m\mathrm{d}T + V_m\mathrm{d}p + S_m\mathrm{d}T - V_m\mathrm{d}p = 0$$

因此，将式(2)中的第 k 个等式去掉，写成

$$\begin{pmatrix} \frac{\partial\mu_1}{\partial x_1} & \frac{\partial\mu_1}{\partial x_2} & \cdots & \frac{\partial\mu_1}{\partial x_{k-1}} \\ \frac{\partial\mu_2}{\partial x_1} & \frac{\partial\mu_2}{\partial x_2} & \cdots & \frac{\partial\mu_2}{\partial x_{k-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial\mu_{k-1}}{\partial x_1} & \frac{\partial\mu_{k-1}}{\partial x_2} & \cdots & \frac{\partial\mu_{k-1}}{\partial x_{k-1}} \end{pmatrix}\begin{pmatrix}\mathrm{d}x_1\\ \mathrm{d}x_2\\ \vdots\\ \mathrm{d}x_{k-1}\end{pmatrix} = \begin{pmatrix}\mathrm{d}\mu_1\\ \mathrm{d}\mu_2\\ \vdots\\ \mathrm{d}\mu_{k-1}\end{pmatrix} + \begin{pmatrix}\bar{S}_1\\ \bar{S}_2\\ \vdots\\ \bar{S}_{k-1}\end{pmatrix}\mathrm{d}T - \begin{pmatrix}\bar{V}_1\\ \bar{V}_2\\ \vdots\\ \bar{V}_{k-1}\end{pmatrix}\mathrm{d}p \tag{3}$$

σ 相的 Gibbs-Duhem 方程及相平衡条件为

$$\sum_{i=1}^{k}x_i^{(\sigma)}\mathrm{d}\mu_i^{(\sigma)} = -S_m^{(\sigma)}\mathrm{d}T + V_m^{(\sigma)}\mathrm{d}p \quad (\sigma=1,2,\cdots,\varphi) \tag{4}$$

$$\mu_i^{(\sigma)} = \mu_i, \quad (\sigma=1,2,\cdots,\varphi) \tag{5}$$

将式(5)代入(4)，得

$$\sum_{i=1}^{k}x_i^{(\sigma)}\mathrm{d}\mu_i = -S_m^{(\sigma)}\mathrm{d}T + V_m^{(\sigma)}\mathrm{d}p$$

或

$$\sum_{i=1}^{k-1}x_i^{(\sigma)}\mathrm{d}\mu_i = -x_k^{(\sigma)}\mathrm{d}\mu_k - S_m^{(\sigma)}\mathrm{d}T + V_m^{(\sigma)}\mathrm{d}p \quad (\sigma=1,2,\cdots,\varphi) \tag{6}$$

设 μ_i 为第一相的化学势（为简便，后面凡涉及第一项的热力学量都不带标记相的右上标），则当 $\sigma=1$ 时，式(6)是恒等式，去掉，写成矩阵形式

$$\begin{pmatrix} x_1^{(2)} & x_2^{(2)} & \cdots & x_{k-1}^{(2)} \\ x_1^{(3)} & x_2^{(3)} & \cdots & x_{k-1}^{(3)} \\ \vdots & \vdots & \vdots & \vdots \\ x_1^{(\varphi)} & x_2^{(\varphi)} & \cdots & x_{k-1}^{(\varphi)} \end{pmatrix}\begin{pmatrix} d\mu_1 \\ d\mu_2 \\ \vdots \\ d\mu_{k-1} \end{pmatrix} = -\begin{pmatrix} x_k^{(2)} \\ x_k^{(3)} \\ \vdots \\ x_k^{(\varphi)} \end{pmatrix} d\mu_k - \begin{pmatrix} S_m^{(2)} \\ S_m^{(3)} \\ \vdots \\ S_m^{(\varphi)} \end{pmatrix} dT + \begin{pmatrix} V_m^{(2)} \\ V_m^{(3)} \\ \vdots \\ V_m^{(\varphi)} \end{pmatrix} dp$$

$$= -\begin{pmatrix} x_k^{(2)} \\ x_k^{(3)} \\ \vdots \\ x_k^{(\varphi)} \end{pmatrix}\left(-\bar{S}_k dT + \bar{V}_k dp + \sum_{j=1}^{k-1} \frac{\partial\mu_k}{\partial x_j} dx_j \right) - \begin{pmatrix} S_m^{(2)} \\ S_m^{(3)} \\ \vdots \\ S_m^{(\varphi)} \end{pmatrix} dT + \begin{pmatrix} V_m^{(2)} \\ V_m^{(3)} \\ \vdots \\ V_m^{(\varphi)} \end{pmatrix} dp$$

$$= -\begin{pmatrix} x_k^{(2)} \\ x_k^{(3)} \\ \vdots \\ x_k^{(\varphi)} \end{pmatrix}\begin{pmatrix} \frac{\partial\mu_k}{\partial x_1} & \frac{\partial\mu_k}{\partial x_2} & \cdots & \frac{\partial\mu_k}{\partial x_{k-1}} \end{pmatrix}\begin{pmatrix} dx_1 \\ dx_2 \\ \vdots \\ dx_{k-1} \end{pmatrix} - \begin{pmatrix} S_m^{(2)} - x_k^{(2)}\bar{S}_k \\ S_m^{(3)} - x_k^{(3)}\bar{S}_k \\ \vdots \\ S_m^{(\varphi)} - x_k^{(\varphi)}\bar{S}_k \end{pmatrix} dT + \begin{pmatrix} V_m^{(2)} - x_k^{(2)}\bar{V}_k \\ V_m^{(3)} - x_k^{(3)}\bar{V}_k \\ \vdots \\ V_m^{(\varphi)} - x_k^{(\varphi)}\bar{V}_k \end{pmatrix} dp$$

$$= -\begin{pmatrix} x_k^{(2)}\frac{\partial\mu_k}{\partial x_1} & x_k^{(2)}\frac{\partial\mu_k}{\partial x_2} & \cdots & x_k^{(2)}\frac{\partial\mu_k}{\partial x_{k-1}} \\ x_k^{(3)}\frac{\partial\mu_k}{\partial x_1} & x_k^{(3)}\frac{\partial\mu_k}{\partial x_2} & \cdots & x_k^{(3)}\frac{\partial\mu_k}{\partial x_{k-1}} \\ \vdots & \vdots & \vdots & \vdots \\ x_k^{(\varphi)}\frac{\partial\mu_k}{\partial x_1} & x_k^{(\varphi)}\frac{\partial\mu_k}{\partial x_2} & \cdots & x_k^{(\varphi)}\frac{\partial\mu_k}{\partial x_{k-1}} \end{pmatrix}\begin{pmatrix} dx_1 \\ dx_2 \\ \vdots \\ dx_{k-1} \end{pmatrix} - \begin{pmatrix} S_m^{(2)} - x_k^{(2)}\bar{S}_k \\ S_m^{(3)} - x_k^{(3)}\bar{S}_k \\ \vdots \\ S_m^{(\varphi)} - x_k^{(\varphi)}\bar{S}_k \end{pmatrix} dT + \begin{pmatrix} V_m^{(2)} - x_k^{(2)}\bar{V}_k \\ V_m^{(3)} - x_k^{(3)}\bar{V}_k \\ \vdots \\ V_m^{(\varphi)} - x_k^{(\varphi)}\bar{V}_k \end{pmatrix} dp \quad (7)$$

将式(3)用于第一相,并左乘式(7)左边的系数矩阵,再将式(7)代入,得

$$\begin{pmatrix} x_1^{(2)} & x_2^{(2)} & \cdots & x_{k-1}^{(2)} \\ x_1^{(3)} & x_2^{(3)} & \cdots & x_{k-1}^{(3)} \\ \vdots & \vdots & \vdots & \vdots \\ x_1^{(\varphi)} & x_2^{(\varphi)} & \cdots & x_{k-1}^{(\varphi)} \end{pmatrix}\begin{pmatrix} \frac{\partial\mu_1}{\partial x_1} & \frac{\partial\mu_1}{\partial x_2} & \cdots & \frac{\partial\mu_1}{\partial x_{k-1}} \\ \frac{\partial\mu_2}{\partial x_1} & \frac{\partial\mu_2}{\partial x_2} & \cdots & \frac{\partial\mu_2}{\partial x_{k-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial\mu_{k-1}}{\partial x_1} & \frac{\partial\mu_{k-1}}{\partial x_2} & \cdots & \frac{\partial\mu_{k-1}}{\partial x_{k-1}} \end{pmatrix}\begin{pmatrix} dx_1 \\ dx_2 \\ \vdots \\ dx_{k-1} \end{pmatrix}$$

$$= -\begin{pmatrix} S_m^{(2)} - x_k^{(2)}\bar{S}_k \\ S_m^{(3)} - x_k^{(3)}\bar{S}_k \\ \vdots \\ S_m^{(\varphi)} - x_k^{(\varphi)}\bar{S}_k \end{pmatrix} dT + \begin{pmatrix} x_1^{(2)} & x_2^{(2)} & \cdots & x_{k-1}^{(2)} \\ x_1^{(3)} & x_2^{(3)} & \cdots & x_{k-1}^{(3)} \\ \vdots & \vdots & \vdots & \vdots \\ x_1^{(\varphi)} & x_2^{(\varphi)} & \cdots & x_{k-1}^{(\varphi)} \end{pmatrix}\begin{pmatrix} \bar{S}_1 \\ \bar{S}_2 \\ \vdots \\ \bar{S}_{k-1} \end{pmatrix} dT + \begin{pmatrix} V_m^{(2)} - x_k^{(2)}\bar{V}_k \\ V_m^{(3)} - x_k^{(3)}\bar{V}_k \\ \vdots \\ V_m^{(\varphi)} - x_k^{(\varphi)}\bar{V}_k \end{pmatrix} dp -$$

$$\begin{pmatrix} x_1^{(2)} & x_2^{(2)} & \cdots & x_{k-1}^{(2)} \\ x_1^{(3)} & x_2^{(3)} & \cdots & x_{k-1}^{(3)} \\ \vdots & \vdots & \vdots & \vdots \\ x_1^{(\varphi)} & x_2^{(\varphi)} & \cdots & x_{k-1}^{(\varphi)} \end{pmatrix}\begin{pmatrix} \bar{V}_1 \\ \bar{V}_2 \\ \vdots \\ \bar{V}_{k-1} \end{pmatrix} dp - \begin{pmatrix} x_k^{(2)}\frac{\partial\mu_k}{\partial x_1} & x_k^{(2)}\frac{\partial\mu_k}{\partial x_2} & \cdots & x_k^{(2)}\frac{\partial\mu_k}{\partial x_{k-1}} \\ x_k^{(3)}\frac{\partial\mu_k}{\partial x_1} & x_k^{(3)}\frac{\partial\mu_k}{\partial x_2} & \cdots & x_k^{(3)}\frac{\partial\mu_k}{\partial x_{k-1}} \\ \vdots & \vdots & \vdots & \vdots \\ x_k^{(\varphi)}\frac{\partial\mu_k}{\partial x_1} & x_k^{(\varphi)}\frac{\partial\mu_k}{\partial x_2} & \cdots & x_k^{(\varphi)}\frac{\partial\mu_k}{\partial x_{k-1}} \end{pmatrix}\begin{pmatrix} dx_1 \\ dx_2 \\ \vdots \\ dx_{k-1} \end{pmatrix} \quad (8)$$

或

$$\begin{pmatrix} \sum_{i=1}^{k} x_i^{(2)} \frac{\partial \mu_i}{\partial x_1} & \sum_{i=1}^{k} x_i^{(2)} \frac{\partial \mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k} x_i^{(2)} \frac{\partial \mu_i}{\partial x_{k-1}} \\ \sum_{i=1}^{k} x_i^{(3)} \frac{\partial \mu_i}{\partial x_1} & \sum_{i=1}^{k} x_i^{(3)} \frac{\partial \mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k} x_i^{(3)} \frac{\partial \mu_i}{\partial x_{k-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \sum_{i=1}^{k} x_i^{(\varphi)} \frac{\partial \mu_i}{\partial x_1} & \sum_{i=1}^{k} x_i^{(\varphi)} \frac{\partial \mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k} x_i^{(\varphi)} \frac{\partial \mu_i}{\partial x_{k-1}} \end{pmatrix} \begin{pmatrix} \mathrm{d}x_1 \\ \mathrm{d}x_2 \\ \vdots \\ \mathrm{d}x_{k-1} \end{pmatrix} = - \begin{pmatrix} S_m^{(2)} - \sum_{i=1}^{k} x_i^{(2)} \overline{S}_i \\ S_m^{(3)} - \sum_{i=1}^{k} x_i^{(3)} \overline{S}_i \\ \vdots \\ S_m^{(\varphi)} - \sum_{i=1}^{k} x_i^{(\varphi)} \overline{S}_i \end{pmatrix} \mathrm{d}T + \begin{pmatrix} V_m^{(2)} - \sum_{i=1}^{k} x_i^{(2)} \overline{V}_i \\ V_m^{(3)} - \sum_{i=1}^{k} x_i^{(3)} \overline{V}_i \\ \vdots \\ V_m^{(\varphi)} - \sum_{i=1}^{k} x_i^{(\varphi)} \overline{V}_i \end{pmatrix} \mathrm{d}p \tag{9}$$

容易证明，这个结果与将式(2)中的第 k 个等式去掉所得结果是一样的.

如果 $\varphi = k+1$，则平衡时体系有一个独立变量；如果选择温度做独立变量，则其他非独立变量都可表示为温度的函数. 事实上，当 $\varphi = k+1$ 时，式(9)是 k 个方程；将式(9)右边第二项移到左边，则可将 $\mathrm{d}x_1, \mathrm{d}x_2, \cdots, \mathrm{d}x_{k-1}, \mathrm{d}p$ 等 k 个微分作为 $\mathrm{d}T$ 的函数解出. 由于每一相都可作为第一相，因此，将第一相和其他相交换位置即可得任一相的浓度微分与温度微分的关系.

如果 $\varphi = k$，则平衡时体系有两个独立变量；如果选择温度和压力做独立变量，则其他非独立变量都可表示为温度和压力的函数. 事实上，如果 $\varphi = k$，式(9)是 $(k-1)$ 个方程，刚好可把 $(k-1)$ 个浓度微分作为温度和压力微分的函数解出.

如果 $2 \leqslant \varphi \leqslant k-1$，则平衡时体系有两个以上的独立变量；如果选择温度、压力和一些浓度做独立变量，则其他非独立变量都可表示为温度、压力和这些浓度的函数. 事实上，式(9)中涉及 $(k+1)$ 个变量：$\mathrm{d}x_i (i = 1, 2, \cdots, k-1)$、$\mathrm{d}p$ 和 $\mathrm{d}T$，若在这 $(k+1)$ 个变量中选温度、压力和 $(k-\varphi)$ 个浓度共 $(k-\varphi+2 = f)$ 个变量做独立变量，则其他非独立变量可用这些独立变量来表示. 为此，将式(9)左边的 $(k-\varphi)$ 个浓度变量移至右边：

$$\begin{pmatrix} \sum_{i=1}^{k} x_i^{(2)} \frac{\partial \mu_i}{\partial x_1} & \sum_{i=1}^{k} x_i^{(2)} \frac{\partial \mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k} x_i^{(2)} \frac{\partial \mu_i}{\partial x_{\varphi-1}} \\ \sum_{i=1}^{k} x_i^{(3)} \frac{\partial \mu_i}{\partial x_1} & \sum_{i=1}^{k} x_i^{(3)} \frac{\partial \mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k} x_i^{(3)} \frac{\partial \mu_i}{\partial x_{\varphi-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \sum_{i=1}^{k} x_i^{(\varphi)} \frac{\partial \mu_i}{\partial x_1} & \sum_{i=1}^{k} x_i^{(\varphi)} \frac{\partial \mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k} x_i^{(\varphi)} \frac{\partial \mu_i}{\partial x_{\varphi-1}} \end{pmatrix} \begin{pmatrix} \mathrm{d}x_1 \\ \mathrm{d}x_2 \\ \vdots \\ \mathrm{d}x_{\varphi-1} \end{pmatrix}$$

$$= - \begin{pmatrix} \sum_{i=1}^{k} x_i^{(2)} \frac{\partial \mu_i}{\partial x_\varphi} & \sum_{i=1}^{k} x_i^{(2)} \frac{\partial \mu_i}{\partial x_{\varphi+1}} & \cdots & \sum_{i=1}^{k} x_i^{(2)} \frac{\partial \mu_i}{\partial x_{k-1}} \\ \sum_{i=1}^{k} x_i^{(3)} \frac{\partial \mu_i}{\partial x_\varphi} & \sum_{i=1}^{k} x_i^{(3)} \frac{\partial \mu_i}{\partial x_{\varphi+1}} & \cdots & \sum_{i=1}^{k} x_i^{(3)} \frac{\partial \mu_i}{\partial x_{k-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \sum_{i=1}^{k} x_i^{(\varphi)} \frac{\partial \mu_i}{\partial x_\varphi} & \sum_{i=1}^{k} x_i^{(\varphi)} \frac{\partial \mu_i}{\partial x_{\varphi+1}} & \cdots & \sum_{i=1}^{k} x_i^{(\varphi)} \frac{\partial \mu_i}{\partial x_{k-1}} \end{pmatrix} \begin{pmatrix} \mathrm{d}x_\varphi \\ \mathrm{d}x_{\varphi+1} \\ \vdots \\ \mathrm{d}x_{k-1} \end{pmatrix} - \begin{pmatrix} S_m^{(2)} - \sum_{i=1}^{k} x_i^{(2)} \overline{S}_i \\ S_m^{(3)} - \sum_{i=1}^{k} x_i^{(3)} \overline{S}_i \\ \vdots \\ S_m^{(\varphi)} - \sum_{i=1}^{k} x_i^{(\varphi)} \overline{S}_i \end{pmatrix} \mathrm{d}T + \begin{pmatrix} V_m^{(2)} - \sum_{i=1}^{k} x_i^{(2)} \overline{V}_i \\ V_m^{(3)} - \sum_{i=1}^{k} x_i^{(3)} \overline{V}_i \\ \vdots \\ V_m^{(\varphi)} - \sum_{i=1}^{k} x_i^{(\varphi)} \overline{V}_i \end{pmatrix} \mathrm{d}p \tag{10}$$

式(10)左边剩$(\varphi-1)$个浓度微分，而式(10)是$(\varphi-1)$个方程，刚好把这$(\varphi-1)$个浓度微分作为独立微分的函数解出来. 解方程组(10)，得

$$
\begin{vmatrix}
\sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{j-1}} & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_j} & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{\varphi-1}} \\
\sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{j-1}} & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_j} & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{\varphi-1}} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{j-1}} & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_j} & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{\varphi-1}}
\end{vmatrix}\mathrm{d}x_j
$$

$$
=-\sum_{l=\varphi}^{k-1}
\begin{vmatrix}
\sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{j-1}} & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_l} & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{\varphi-1}} \\
\sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{j-1}} & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_l} & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{\varphi-1}} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{j-1}} & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_l} & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{\varphi-1}}
\end{vmatrix}\mathrm{d}x_l\ -
$$

$$
\begin{vmatrix}
\sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{j-1}} & S_m^{(2)}-\sum_{i=1}^{k}x_i^{(2)}\bar{S}_i & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{\varphi-1}} \\
\sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{j-1}} & S_m^{(3)}-\sum_{i=1}^{k}x_i^{(3)}\bar{S}_i & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{\varphi-1}} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{j-1}} & S_m^{(\varphi)}-\sum_{i=1}^{k}x_i^{(\varphi)}\bar{S}_i & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{\varphi-1}}
\end{vmatrix}\mathrm{d}T\ +
$$

$$
\begin{vmatrix}
\sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{j-1}} & V_m^{(2)}-\sum_{i=1}^{k}x_i^{(2)}\bar{V}_i & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(2)}\frac{\partial\mu_i}{\partial x_{\varphi-1}} \\
\sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{j-1}} & V_m^{(3)}-\sum_{i=1}^{k}x_i^{(3)}\bar{V}_i & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(3)}\frac{\partial\mu_i}{\partial x_{\varphi-1}} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_1} & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_2} & \cdots & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{j-1}} & V_m^{(\varphi)}-\sum_{i=1}^{k}x_i^{(\varphi)}\bar{V}_i & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{j+1}} & \cdots & \sum_{i=1}^{k}x_i^{(\varphi)}\frac{\partial\mu_i}{\partial x_{\varphi-1}}
\end{vmatrix}\mathrm{d}p
$$

$$(j=1,2,\cdots,\varphi-1) \qquad (11)$$

式(11)就是k组分和φ相$(2\leqslant\varphi\leqslant k-1)$的多元复相平衡体系第一相的非独立变量$x_1,x_2,\cdots,x_{\varphi-1}$和独立变量$x_\varphi,x_{\varphi+1},\cdots,x_{k-1}$, T,p之间的微分关系.

将式(11)中的四个行列式依次用$\Delta,\Delta_{j,l},\Delta_{j,T}$, $\Delta_{j,p}$表示，而将式(11)简写为

$$\Delta\mathrm{d}x_j=-\sum_{l=\varphi}^{k-1}\Delta_{j,l}\mathrm{d}x_l-\Delta_{j,T}\mathrm{d}T+\Delta_{j,p}\mathrm{d}p$$

$$(j=1,2,\cdots,\varphi-1) \qquad (12)$$

或

$$
\begin{pmatrix}\mathrm{d}x_1\\ \mathrm{d}x_2\\ \vdots\\ \mathrm{d}x_{\varphi-1}\end{pmatrix}=-\frac{1}{\Delta}
\begin{pmatrix}
\Delta_{1,\varphi} & \Delta_{1,\varphi+1} & \cdots & \Delta_{1,k-1}\\
\Delta_{2,\varphi} & \Delta_{2,\varphi+1} & \cdots & \Delta_{2,k-1}\\
\vdots & \vdots & \vdots & \vdots\\
\Delta_{\varphi-1,\varphi} & \Delta_{\varphi-1,\varphi+1} & \cdots & \Delta_{\varphi-1,k-1}
\end{pmatrix}\times
$$

$$\begin{pmatrix} dx_{\varphi} \\ dx_{\varphi+1} \\ \vdots \\ dx_{k-1} \end{pmatrix} - \frac{1}{\Delta}\begin{pmatrix} \Delta_{1,T} \\ \Delta_{2,T} \\ \vdots \\ \Delta_{\varphi-1,T} \end{pmatrix} dT + \frac{1}{\Delta}\begin{pmatrix} \Delta_{1,p} \\ \Delta_{2,p} \\ \vdots \\ \Delta_{\varphi-1,p} \end{pmatrix} dp \quad (13)$$

3　其他相非独立和独立变量间的微分关系

由式(3)可知，对 $\sigma(\sigma=2,3,\cdots,\varphi)$ 相，有

$$\begin{pmatrix} \frac{\partial \mu_1^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_1^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_1^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \frac{\partial \mu_2^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_2^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_2^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \end{pmatrix}\begin{pmatrix} dx_1^{(\sigma)} \\ dx_2^{(\sigma)} \\ \vdots \\ dx_{k-1}^{(\sigma)} \end{pmatrix} - \begin{pmatrix} \bar{S}_1^{(\sigma)} \\ \bar{S}_2^{(\sigma)} \\ \vdots \\ \bar{S}_{k-1}^{(\sigma)} \end{pmatrix} dT + \begin{pmatrix} \bar{V}_1^{(\sigma)} \\ \bar{V}_2^{(\sigma)} \\ \vdots \\ \bar{V}_{k-1}^{(\sigma)} \end{pmatrix} dp = \begin{pmatrix} d\mu_1^{(\sigma)} \\ d\mu_2^{(\sigma)} \\ \vdots \\ d\mu_{k-1}^{(\sigma)} \end{pmatrix} \quad (14)$$

由式(5)可知，式(3)和(14)中两个化学势的列矩阵相等，所以

$$\begin{pmatrix} \frac{\partial \mu_1^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_1^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_1^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \frac{\partial \mu_2^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_2^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_2^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \end{pmatrix}\begin{pmatrix} dx_1^{(\sigma)} \\ dx_2^{(\sigma)} \\ \vdots \\ dx_{k-1}^{(\sigma)} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{\partial \mu_1}{\partial x_1} & \frac{\partial \mu_1}{\partial x_2} & \cdots & \frac{\partial \mu_1}{\partial x_{k-1}} \\ \frac{\partial \mu_2}{\partial x_1} & \frac{\partial \mu_2}{\partial x_2} & \cdots & \frac{\partial \mu_2}{\partial x_{k-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial \mu_{k-1}}{\partial x_1} & \frac{\partial \mu_{k-1}}{\partial x_2} & \cdots & \frac{\partial \mu_{k-1}}{\partial x_{k-1}} \end{pmatrix}\begin{pmatrix} dx_1 \\ dx_2 \\ \vdots \\ dx_{k-1} \end{pmatrix} - \begin{pmatrix} \bar{S}_1 - \bar{S}_1^{(\sigma)} \\ \bar{S}_2 - \bar{S}_2^{(\sigma)} \\ \vdots \\ \bar{S}_{k-1} - \bar{S}_{k-1}^{(\sigma)} \end{pmatrix} dT + \begin{pmatrix} \bar{V}_1 - \bar{V}_1^{(\sigma)} \\ \bar{V}_2 - \bar{V}_2^{(\sigma)} \\ \vdots \\ \bar{V}_{k-1} - \bar{V}_{k-1}^{(\sigma)} \end{pmatrix} dp \quad (15)$$

将式(15)右边第一个矩阵拆分成两个，得

$$\begin{pmatrix} \frac{\partial \mu_1^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_1^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_1^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \frac{\partial \mu_2^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_2^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_2^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \end{pmatrix}\begin{pmatrix} dx_1^{(\sigma)} \\ dx_2^{(\sigma)} \\ \vdots \\ dx_{k-1}^{(\sigma)} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{\partial \mu_1}{\partial x_1} & \frac{\partial \mu_1}{\partial x_2} & \cdots & \frac{\partial \mu_1}{\partial x_{\varphi-1}} \\ \frac{\partial \mu_2}{\partial x_1} & \frac{\partial \mu_2}{\partial x_2} & \cdots & \frac{\partial \mu_2}{\partial x_{\varphi-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial \mu_{k-1}}{\partial x_1} & \frac{\partial \mu_{k-1}}{\partial x_2} & \cdots & \frac{\partial \mu_{k-1}}{\partial x_{\varphi-1}} \end{pmatrix}\begin{pmatrix} dx_1 \\ dx_2 \\ \vdots \\ dx_{\varphi-1} \end{pmatrix} + \begin{pmatrix} \frac{\partial \mu_1}{\partial x_{\varphi}} & \frac{\partial \mu_1}{\partial x_{\varphi+1}} & \cdots & \frac{\partial \mu_1}{\partial x_{k-1}} \\ \frac{\partial \mu_2}{\partial x_{\varphi}} & \frac{\partial \mu_2}{\partial x_{\varphi+1}} & \cdots & \frac{\partial \mu_2}{\partial x_{k-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial \mu_{k-1}}{\partial x_{\varphi}} & \frac{\partial \mu_{k-1}}{\partial x_{\varphi+1}} & \cdots & \frac{\partial \mu_{k-1}}{\partial x_{k-1}} \end{pmatrix}\begin{pmatrix} dx_{\varphi} \\ dx_{\varphi+1} \\ \vdots \\ dx_{k-1} \end{pmatrix} - \begin{pmatrix} \bar{S}_1 - \bar{S}_1^{(\sigma)} \\ \bar{S}_2 - \bar{S}_2^{(\sigma)} \\ \vdots \\ \bar{S}_{k-1} - \bar{S}_{k-1}^{(\sigma)} \end{pmatrix} dT + \begin{pmatrix} \bar{V}_1 - \bar{V}_1^{(\sigma)} \\ \bar{V}_2 - \bar{V}_2^{(\sigma)} \\ \vdots \\ \bar{V}_{k-1} - \bar{V}_{k-1}^{(\sigma)} \end{pmatrix} dp \quad (16)$$

将式(13)代入式(16)，得

$$\begin{pmatrix} \frac{\partial \mu_1^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_1^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_1^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \frac{\partial \mu_2^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_2^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_2^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial \mu_{k-1}^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \end{pmatrix}\begin{pmatrix} dx_1^{(\sigma)} \\ dx_2^{(\sigma)} \\ \vdots \\ dx_{k-1}^{(\sigma)} \end{pmatrix}$$

$$= -\frac{1}{\Delta}\begin{pmatrix} \frac{\partial \mu_1}{\partial x_1} & \frac{\partial \mu_1}{\partial x_2} & \cdots & \frac{\partial \mu_1}{\partial x_{\varphi-1}} \\ \frac{\partial \mu_2}{\partial x_1} & \frac{\partial \mu_2}{\partial x_2} & \cdots & \frac{\partial \mu_2}{\partial x_{\varphi-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial \mu_{k-1}}{\partial x_1} & \frac{\partial \mu_{k-1}}{\partial x_2} & \cdots & \frac{\partial \mu_{k-1}}{\partial x_{\varphi-1}} \end{pmatrix} \times$$

$$\begin{pmatrix} \Delta_{1,\varphi} & \Delta_{1,\varphi+1} & \cdots & \Delta_{1,k-1} \\ \Delta_{2,\varphi} & \Delta_{2,\varphi+1} & \cdots & \Delta_{2,k-1} \\ \vdots & \vdots & \vdots & \vdots \\ \Delta_{\varphi-1,\varphi} & \Delta_{\varphi-1,\varphi+1} & \cdots & \Delta_{\varphi-1,k-1} \end{pmatrix}\begin{pmatrix} dx_\varphi \\ dx_{\varphi+1} \\ \vdots \\ dx_{k-1} \end{pmatrix} + \begin{pmatrix} \frac{\partial\mu_1}{\partial x_\varphi} & \frac{\partial\mu_1}{\partial x_{\varphi+1}} & \cdots & \frac{\partial\mu_1}{\partial x_{k-1}} \\ \frac{\partial\mu_2}{\partial x_\varphi} & \frac{\partial\mu_2}{\partial x_{\varphi+1}} & \cdots & \frac{\partial\mu_2}{\partial x_{k-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial\mu_{k-1}}{\partial x_\varphi} & \frac{\partial\mu_{k-1}}{\partial x_{\varphi+1}} & \cdots & \frac{\partial\mu_{k-1}}{\partial x_{k-1}} \end{pmatrix}\begin{pmatrix} dx_\varphi \\ dx_{\varphi+1} \\ \vdots \\ dx_{k-1} \end{pmatrix} - \begin{pmatrix} \bar{S}_1 - \bar{S}_1^{(\sigma)} \\ \bar{S}_2 - \bar{S}_2^{(\sigma)} \\ \vdots \\ \bar{S}_{k-1} - \bar{S}_{k-1}^{(\sigma)} \end{pmatrix} dT -$$

$$\frac{1}{\Delta}\begin{pmatrix} \frac{\partial\mu_1}{\partial x_1} & \frac{\partial\mu_1}{\partial x_2} & \cdots & \frac{\partial\mu_1}{\partial x_{\varphi-1}} \\ \frac{\partial\mu_2}{\partial x_1} & \frac{\partial\mu_2}{\partial x_2} & \cdots & \frac{\partial\mu_2}{\partial x_{\varphi-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial\mu_{k-1}}{\partial x_1} & \frac{\partial\mu_{k-1}}{\partial x_2} & \cdots & \frac{\partial\mu_{k-1}}{\partial x_{\varphi-1}} \end{pmatrix}\begin{pmatrix} \Delta_{1,T} \\ \Delta_{2,T} \\ \vdots \\ \Delta_{\varphi-1,T} \end{pmatrix} dT + \begin{pmatrix} \bar{V}_1 - \bar{V}_1^{(\sigma)} \\ \bar{V}_2 - \bar{V}_2^{(\sigma)} \\ \vdots \\ \bar{V}_{k-1} - \bar{V}_{k-1}^{(\sigma)} \end{pmatrix} dp + \frac{1}{\Delta}\begin{pmatrix} \frac{\partial\mu_1}{\partial x_1} & \frac{\partial\mu_1}{\partial x_2} & \cdots & \frac{\partial\mu_1}{\partial x_{\varphi-1}} \\ \frac{\partial\mu_2}{\partial x_1} & \frac{\partial\mu_2}{\partial x_2} & \cdots & \frac{\partial\mu_2}{\partial x_{\varphi-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial\mu_{k-1}}{\partial x_1} & \frac{\partial\mu_{k-1}}{\partial x_2} & \cdots & \frac{\partial\mu_{k-1}}{\partial x_{\varphi-1}} \end{pmatrix}\begin{pmatrix} \Delta_{1,p} \\ \Delta_{2,p} \\ \vdots \\ \Delta_{\varphi-1,p} \end{pmatrix} dp$$

$$= -\frac{1}{\Delta}\begin{pmatrix} \sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\Delta_{j,\varphi} & \sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\Delta_{j,\varphi+1} & \cdots & \sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\Delta_{j,k-1} \\ \sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\Delta_{j,\varphi} & \sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\Delta_{j,\varphi+1} & \cdots & \sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\Delta_{j,k-1} \\ \vdots & \vdots & \vdots & \vdots \\ \sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\Delta_{j,\varphi} & \sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\Delta_{j,\varphi+1} & \cdots & \sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\Delta_{j,k-1} \end{pmatrix}\begin{pmatrix} dx_\varphi \\ dx_{\varphi+1} \\ \vdots \\ dx_{k-1} \end{pmatrix} + \begin{pmatrix} \frac{\partial\mu_1}{\partial x_\varphi} & \frac{\partial\mu_1}{\partial x_{\varphi+1}} & \cdots & \frac{\partial\mu_1}{\partial x_{k-1}} \\ \frac{\partial\mu_2}{\partial x_\varphi} & \frac{\partial\mu_2}{\partial x_{\varphi+1}} & \cdots & \frac{\partial\mu_2}{\partial x_{k-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial\mu_{k-1}}{\partial x_\varphi} & \frac{\partial\mu_{k-1}}{\partial x_{\varphi+1}} & \cdots & \frac{\partial\mu_{k-1}}{\partial x_{k-1}} \end{pmatrix} \times$$

$$\begin{pmatrix} dx_\varphi \\ dx_{\varphi+1} \\ \vdots \\ dx_{k-1} \end{pmatrix} - \begin{pmatrix} \bar{S}_1 - \bar{S}_1^{(\sigma)} \\ \bar{S}_2 - \bar{S}_2^{(\sigma)} \\ \vdots \\ \bar{S}_{k-1} - \bar{S}_{k-1}^{(\sigma)} \end{pmatrix} dT - \frac{1}{\Delta}\begin{pmatrix} \sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\Delta_{j,T} \\ \sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\Delta_{j,T} \\ \vdots \\ \sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\Delta_{j,T} \end{pmatrix} dT + \begin{pmatrix} \bar{V}_1 - \bar{V}_1^{(\sigma)} \\ \bar{V}_2 - \bar{V}_2^{(\sigma)} \\ \vdots \\ \bar{V}_{k-1} - \bar{V}_{k-1}^{(\sigma)} \end{pmatrix} dp + \frac{1}{\Delta}\begin{pmatrix} \sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\Delta_{j,p} \\ \sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\Delta_{j,p} \\ \vdots \\ \sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\Delta_{j,p} \end{pmatrix} dp$$

即

$$\begin{pmatrix} \frac{\partial\mu_1^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_1^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \frac{\partial\mu_2^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_2^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \end{pmatrix}\begin{pmatrix} dx_1^{(\sigma)} \\ dx_2^{(\sigma)} \\ \vdots \\ dx_{k-1}^{(\sigma)} \end{pmatrix} =$$

$$
=\begin{pmatrix}
\frac{\partial\mu_1}{\partial x_\varphi}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\frac{\Delta_{j,\varphi}}{\Delta} & \frac{\partial\mu_1}{\partial x_{\varphi+1}}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\frac{\Delta_{j,\varphi+1}}{\Delta} & \cdots & \frac{\partial\mu_1}{\partial x_{k-1}}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\frac{\Delta_{j,k-1}}{\Delta}\\
\frac{\partial\mu_2}{\partial x_\varphi}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\frac{\Delta_{j,\varphi}}{\Delta} & \frac{\partial\mu_2}{\partial x_{\varphi+1}}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\frac{\Delta_{j,\varphi+1}}{\Delta} & \cdots & \frac{\partial\mu_2}{\partial x_{k-1}}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\frac{\Delta_{j,k-1}}{\Delta}\\
\vdots & \vdots & \vdots & \vdots\\
\frac{\partial\mu_{k-1}}{\partial x_\varphi}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\frac{\Delta_{j,\varphi}}{\Delta} & \frac{\partial\mu_{k-1}}{\partial x_{\varphi+1}}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\frac{\Delta_{j,\varphi+1}}{\Delta} & \cdots & \frac{\partial\mu_{k-1}}{\partial x_{k-1}}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\frac{\Delta_{j,k-1}}{\Delta}
\end{pmatrix}\times
$$

$$
\begin{pmatrix}\mathrm{d}x_\varphi\\ \mathrm{d}x_{\varphi+1}\\ \vdots\\ \mathrm{d}x_{k-1}\end{pmatrix}-
\begin{pmatrix}
\bar{S}_1-\bar{S}_1^{(\sigma)}+\sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\frac{\Delta_{j,T}}{\Delta}\\
\bar{S}_2-\bar{S}_2^{(\sigma)}+\sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\frac{\Delta_{j,T}}{\Delta}\\
\vdots\\
\bar{S}_{k-1}-\bar{S}_{k-1}^{(\sigma)}+\sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\frac{\Delta_{j,T}}{\Delta}
\end{pmatrix}\mathrm{d}T+
\begin{pmatrix}
\bar{V}_1-\bar{V}_1^{(\sigma)}+\sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\frac{\Delta_{j,p}}{\Delta}\\
\bar{V}_2-\bar{V}_2^{(\sigma)}+\sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\frac{\Delta_{j,p}}{\Delta}\\
\vdots\\
\bar{V}_{k-1}-\bar{V}_{k-1}^{(\sigma)}+\sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\frac{\Delta_{j,p}}{\Delta}
\end{pmatrix}\mathrm{d}p \qquad (17)
$$

解式(17)，得：

$$
\begin{vmatrix}
\frac{\partial\mu_1^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_1^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \frac{\partial\mu_1^{(\sigma)}}{\partial x_i^{(\sigma)}} & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}}\\
\frac{\partial\mu_2^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_2^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \frac{\partial\mu_2^{(\sigma)}}{\partial x_i^{(\sigma)}} & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}}\\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots\\
\frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_i^{(\sigma)}} & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}}
\end{vmatrix}\mathrm{d}x_i^{(\sigma)}
$$

$$
=\sum_{l=\varphi}^{k-1}\begin{vmatrix}
\frac{\partial\mu_1^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_1^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \frac{\partial\mu_1}{\partial x_l}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\frac{\Delta_{j,l}}{\Delta} & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}}\\
\frac{\partial\mu_2^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_2^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \frac{\partial\mu_2}{\partial x_l}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\frac{\Delta_{j,l}}{\Delta} & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}}\\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots\\
\frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \frac{\partial\mu_{k-1}}{\partial x_l}-\sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\frac{\Delta_{j,l}}{\Delta} & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}}
\end{vmatrix}\mathrm{d}x_l-
$$

$$
\begin{vmatrix}
\frac{\partial\mu_1^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_1^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \bar{S}_1-\bar{S}_1^{(\sigma)}+\sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\frac{\Delta_{j,T}}{\Delta} & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}}\\
\frac{\partial\mu_2^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_2^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \bar{S}_2-\bar{S}_2^{(\sigma)}+\sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\frac{\Delta_{j,T}}{\Delta} & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}}\\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots\\
\frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \bar{S}_{k-1}-\bar{S}_{k-1}^{(\sigma)}+\sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\frac{\Delta_{j,T}}{\Delta} & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}}
\end{vmatrix}\mathrm{d}T+
$$

$$\begin{vmatrix} \frac{\partial\mu_1^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_1^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \bar{V}_1 - \bar{V}_1^{(\sigma)} + \sum_{j=1}^{\varphi-1}\frac{\partial\mu_1}{\partial x_j}\frac{\Delta_{j,p}}{\Delta} & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_1^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \frac{\partial\mu_2^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_2^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \bar{V}_2 - \bar{V}_2^{(\sigma)} + \sum_{j=1}^{\varphi-1}\frac{\partial\mu_2}{\partial x_j}\frac{\Delta_{j,p}}{\Delta} & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_2^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_1^{(\sigma)}} & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_2^{(\sigma)}} & \cdots & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{i-1}^{(\sigma)}} & \bar{V}_{k-1} - \bar{V}_{k-1}^{(\sigma)} + \sum_{j=1}^{\varphi-1}\frac{\partial\mu_{k-1}}{\partial x_j}\frac{\Delta_{j,p}}{\Delta} & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{i+1}^{(\sigma)}} & \cdots & \frac{\partial\mu_{k-1}^{(\sigma)}}{\partial x_{k-1}^{(\sigma)}} \end{vmatrix} \mathrm{d}p$$

$$(i = 1,2,\cdots,k-1, \quad \sigma = 2,3,\cdots,\varphi) \tag{18}$$

这就是非独立变量 $x_1^{(\sigma)}, x_2^{(\sigma)}, \cdots, x_{k-1}^{(\sigma)}$ ($\sigma = 2,3,\cdots,\varphi$) 与独立变量 $x_\varphi, x_{\varphi+1}, \cdots, x_{k-1}, T, p$ 间微分关系.

4 稳定平衡的结果

由平衡的稳定性理论可证明,式(18)左边的行列式大于0. 恒温恒压下,

$$\begin{aligned} \mathrm{d}\mu_i &= \sum_{j=1}^{k}\frac{\partial\mu_i}{\partial n_j}\mathrm{d}n_j = \sum_{j=1}^{k}\frac{\partial\mu_i}{\partial n_j}\mathrm{d}(x_j n) \\ &= n\sum_{j=1}^{k}\frac{\partial\mu_i}{\partial n_j}\mathrm{d}x_j + \sum_{j=1}^{k}x_j\frac{\partial\mu_i}{\partial n_j}\mathrm{d}n \\ &= n\sum_{j=1}^{k}\frac{\partial\mu_i}{\partial n_j}\mathrm{d}x_j \\ &= n\sum_{j=1}^{k-1}\frac{\partial\mu_i}{\partial n_j}\mathrm{d}x_j + n\frac{\partial\mu_i}{\partial n_k}\mathrm{d}x_k \\ &= n\sum_{j=1}^{k-1}\frac{\partial\mu_i}{\partial n_j}\mathrm{d}x_j - n\frac{\partial\mu_i}{\partial n_k}\sum_{j=1}^{k-1}\mathrm{d}x_j \\ &= n\sum_{j=1}^{k-1}\left(\frac{\partial\mu_i}{\partial n_j} - \frac{\partial\mu_i}{\partial n_k}\right)\mathrm{d}x_j \end{aligned} \tag{19}$$

上面推导过程利用了 Gibbs-Duhem 方程

$$\sum_{j=1}^{k}x_j\frac{\partial\mu_i}{\partial n_j} = 0$$

所以,

$$\frac{\partial\mu_i}{\partial x_j} = n\left(\frac{\partial\mu_i}{\partial n_j} - \frac{\partial\mu_i}{\partial n_k}\right)$$

$$(j = 1,2,\cdots,k-1)$$

$$(i = 1,2,\cdots,k) \tag{20}$$

使用式(20),式(18)左边略去上标 σ 为:

$$\begin{vmatrix} \frac{\partial\mu_1}{\partial x_1} & \frac{\partial\mu_1}{\partial x_2} & \cdots & \frac{\partial\mu_1}{\partial x_{k-1}} \\ \frac{\partial\mu_2}{\partial x_1} & \frac{\partial\mu_2}{\partial x_2} & \cdots & \frac{\partial\mu_2}{\partial x_{k-1}} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial\mu_{k-1}}{\partial x_1} & \frac{\partial\mu_{k-1}}{\partial x_2} & \cdots & \frac{\partial\mu_{k-1}}{\partial x_{k-1}} \end{vmatrix} = n^{k-1}\begin{vmatrix} \frac{\partial\mu_1}{\partial n_1} - \frac{\partial\mu_1}{\partial n_k} & \frac{\partial\mu_1}{\partial n_2} - \frac{\partial\mu_1}{\partial n_k} & \cdots & \frac{\partial\mu_1}{\partial n_{k-2}} - \frac{\partial\mu_1}{\partial n_k} & \frac{\partial\mu_1}{\partial n_{k-1}} - \frac{\partial\mu_1}{\partial n_k} \\ \frac{\partial\mu_2}{\partial n_1} - \frac{\partial\mu_2}{\partial n_k} & \frac{\partial\mu_2}{\partial n_2} - \frac{\partial\mu_2}{\partial n_k} & \cdots & \frac{\partial\mu_2}{\partial n_{k-2}} - \frac{\partial\mu_2}{\partial n_k} & \frac{\partial\mu_2}{\partial n_{k-1}} - \frac{\partial\mu_2}{\partial n_k} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{\partial\mu_{k-1}}{\partial n_1} - \frac{\partial\mu_{k-1}}{\partial n_k} & \frac{\partial\mu_{k-1}}{\partial n_2} - \frac{\partial\mu_{k-1}}{\partial n_k} & \cdots & \frac{\partial\mu_{k-1}}{\partial n_{k-2}} - \frac{\partial\mu_{k-1}}{\partial n_k} & \frac{\partial\mu_{k-1}}{\partial n_{k-1}} - \frac{\partial\mu_{k-1}}{\partial n_k} \end{vmatrix}$$

$$= \frac{n^{k-1}}{\prod_{i=1}^{k-1}n_i} \times \begin{vmatrix} n_1\frac{\partial\mu_1}{\partial n_1} - n_1\frac{\partial\mu_1}{\partial n_k} & \cdots & n_{k-2}\frac{\partial\mu_1}{\partial n_{k-2}} - n_{k-2}\frac{\partial\mu_1}{\partial n_k} & n_{k-1}\frac{\partial\mu_1}{\partial n_{k-1}} - n_{k-1}\frac{\partial\mu_1}{\partial n_k} \\ n_1\frac{\partial\mu_2}{\partial n_1} - n_1\frac{\partial\mu_2}{\partial n_k} & \cdots & n_{k-2}\frac{\partial\mu_2}{\partial n_{k-2}} - n_{k-2}\frac{\partial\mu_2}{\partial n_k} & n_{k-1}\frac{\partial\mu_2}{\partial n_{k-1}} - n_{k-1}\frac{\partial\mu_2}{\partial n_k} \\ \vdots & \vdots & \vdots & \vdots \\ n_1\frac{\partial\mu_{k-1}}{\partial n_1} - n_1\frac{\partial\mu_{k-1}}{\partial n_k} & \cdots & n_{k-2}\frac{\partial\mu_{k-1}}{\partial n_{k-2}} - n_{k-2}\frac{\partial\mu_{k-1}}{\partial n_k} & n_{k-1}\frac{\partial\mu_{k-1}}{\partial n_{k-1}} - n_{k-1}\frac{\partial\mu_{k-1}}{\partial n_k} \end{vmatrix}$$

(各列加于最后一列,并利用 $\sum_{j=1}^{k}n_j\frac{\partial\mu_i}{\partial n_j} = 0$)

$$= \frac{n^{k-1}}{\prod_{t=1}^{k-1} n_t} \times \begin{vmatrix} n_1 \frac{\partial \mu_1}{\partial n_1} - n_1 \frac{\partial \mu_1}{\partial n_k} & \cdots & n_{k-2} \frac{\partial \mu_1}{\partial n_{k-2}} - n_{k-2} \frac{\partial \mu_1}{\partial n_k} & - n_k \frac{\partial \mu_1}{\partial n_k} - (n - n_k) \frac{\partial \mu_1}{\partial n_k} \\ n_1 \frac{\partial \mu_2}{\partial n_1} - n_1 \frac{\partial \mu_2}{\partial n_k} & \cdots & n_{k-2} \frac{\partial \mu_2}{\partial n_{k-2}} - n_{k-2} \frac{\partial \mu_2}{\partial n_k} & - n_k \frac{\partial \mu_2}{\partial n_k} - (n - n_k) \frac{\partial \mu_2}{\partial n_k} \\ \vdots & \vdots & \vdots & \vdots \\ n_1 \frac{\partial \mu_{k-1}}{\partial n_1} - n_1 \frac{\partial \mu_{k-1}}{\partial n_k} & \cdots & n_{k-2} \frac{\partial \mu_{k-1}}{\partial n_{k-2}} - n_{k-2} \frac{\partial \mu_{k-1}}{\partial n_k} & - n_k \frac{\partial \mu_{k-1}}{\partial n_k} - (n - n_k) \frac{\partial \mu_{k-1}}{\partial n_k} \end{vmatrix}$$

$$= \frac{n^{k-1}}{\prod_{t=1}^{k-1} n_t} \times \begin{vmatrix} n_1 \frac{\partial \mu_1}{\partial n_1} - n_1 \frac{\partial \mu_1}{\partial n_k} & n_2 \frac{\partial \mu_1}{\partial n_2} - n_2 \frac{\partial \mu_1}{\partial n_k} & \cdots & n_{k-2} \frac{\partial \mu_1}{\partial n_{k-2}} - n_{k-2} \frac{\partial \mu_1}{\partial n_k} & - n \frac{\partial \mu_1}{\partial n_k} \\ n_1 \frac{\partial \mu_2}{\partial n_1} - n_1 \frac{\partial \mu_2}{\partial n_k} & n_2 \frac{\partial \mu_2}{\partial n_2} - n_2 \frac{\partial \mu_2}{\partial n_k} & \cdots & n_{k-2} \frac{\partial \mu_2}{\partial n_{k-2}} - n_{k-2} \frac{\partial \mu_2}{\partial n_k} & - n \frac{\partial \mu_2}{\partial n_k} \\ \vdots & \vdots & \vdots & \vdots \\ n_1 \frac{\partial \mu_{k-1}}{\partial n_1} - n_1 \frac{\partial \mu_{k-1}}{\partial n_k} & n_2 \frac{\partial \mu_{k-1}}{\partial n_2} - n_2 \frac{\partial \mu_{k-1}}{\partial n_k} & \cdots & n_{k-2} \frac{\partial \mu_{k-1}}{\partial n_{k-2}} - n_{k-2} \frac{\partial \mu_{k-1}}{\partial n_k} & - n \frac{\partial \mu_{k-1}}{\partial n_k} \end{vmatrix}$$

$$= - \frac{n^k}{n_{k-1}} \begin{vmatrix} \frac{\partial \mu_1}{\partial n_1} - \frac{\partial \mu_1}{\partial n_k} & \frac{\partial \mu_1}{\partial n_2} - \frac{\partial \mu_1}{\partial n_k} & \cdots & \frac{\partial \mu_1}{\partial n_{k-2}} - \frac{\partial \mu_1}{\partial n_k} & \frac{\partial \mu_1}{\partial n_k} \\ \frac{\partial \mu_2}{\partial n_1} - \frac{\partial \mu_2}{\partial n_k} & \frac{\partial \mu_2}{\partial n_2} - \frac{\partial \mu_2}{\partial n_k} & \cdots & \frac{\partial \mu_2}{\partial n_{k-2}} - \frac{\partial \mu_2}{\partial n_k} & \frac{\partial \mu_2}{\partial n_k} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial \mu_{k-1}}{\partial n_1} - \frac{\partial \mu_{k-1}}{\partial n_k} & \frac{\partial \mu_{k-1}}{\partial n_2} - \frac{\partial \mu_{k-1}}{\partial n_k} & \cdots & \frac{\partial \mu_{k-1}}{\partial n_{k-2}} - \frac{\partial \mu_{k-1}}{\partial n_k} & \frac{\partial \mu_{k-1}}{\partial n_k} \end{vmatrix} \quad \text{（最后一列加于其他各列）}$$

$$= - \frac{n^k}{n_{k-1}} \begin{vmatrix} \frac{\partial \mu_1}{\partial n_1} & \frac{\partial \mu_1}{\partial n_2} & \cdots & \frac{\partial \mu_1}{\partial n_{k-2}} & \frac{\partial \mu_1}{\partial n_k} \\ \frac{\partial \mu_2}{\partial n_1} & \frac{\partial \mu_2}{\partial n_2} & \cdots & \frac{\partial \mu_2}{\partial n_{k-2}} & \frac{\partial \mu_2}{\partial n_k} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial \mu_{k-1}}{\partial n_1} & \frac{\partial \mu_{k-1}}{\partial n_2} & \cdots & \frac{\partial \mu_{k-1}}{\partial n_{k-2}} & \frac{\partial \mu_{k-1}}{\partial n_k} \end{vmatrix}$$

$$= - \frac{n^k}{\prod_{i=1}^{k} n_i} \times \begin{vmatrix} n_1 \frac{\partial \mu_1}{\partial n_1} & n_2 \frac{\partial \mu_1}{\partial n_2} & \cdots & n_{k-2} \frac{\partial \mu_1}{\partial n_{k-2}} & n_k \frac{\partial \mu_1}{\partial n_k} \\ n_1 \frac{\partial \mu_2}{\partial n_1} & n_2 \frac{\partial \mu_2}{\partial n_2} & \cdots & n_{k-2} \frac{\partial \mu_2}{\partial n_{k-2}} & n_k \frac{\partial \mu_2}{\partial n_k} \\ \vdots & \vdots & \vdots & \vdots \\ n_1 \frac{\partial \mu_{k-1}}{\partial n_1} & n_2 \frac{\partial \mu_{k-1}}{\partial n_2} & \cdots & n_{k-2} \frac{\partial \mu_{k-1}}{\partial n_{k-2}} & n_k \frac{\partial \mu_{k-1}}{\partial n_k} \end{vmatrix} \quad \left(\begin{array}{l} \text{各列加于最后一列，} \\ \text{再利用} \sum_{j=1}^{k} n_j \frac{\partial \mu_i}{\partial n_j} = 0 \end{array} \right)$$

$$
= -\frac{n^k}{\prod_{i=1}^{k} n_i} \times \begin{vmatrix} n_1 \frac{\partial \mu_1}{\partial n_1} & n_2 \frac{\partial \mu_1}{\partial n_2} & \cdots & n_{k-2} \frac{\partial \mu_1}{\partial n_{k-2}} & -n_{k-1} \frac{\partial \mu_1}{\partial n_{k-1}} \\ n_1 \frac{\partial \mu_2}{\partial n_1} & n_2 \frac{\partial \mu_2}{\partial n_2} & \cdots & n_{k-2} \frac{\partial \mu_2}{\partial n_{k-2}} & -n_{k-1} \frac{\partial \mu_2}{\partial n_{k-1}} \\ \vdots & \vdots & \vdots & \vdots & \\ n_1 \frac{\partial \mu_{k-1}}{\partial n_1} & n_2 \frac{\partial \mu_{k-1}}{\partial n_2} & \cdots & n_{k-2} \frac{\partial \mu_{k-1}}{\partial n_{k-2}} & -n_{k-1} \frac{\partial \mu_{k-1}}{\partial n_{k-1}} \end{vmatrix}
$$

$$
= \frac{n^k}{n_k} \begin{vmatrix} \frac{\partial \mu_1}{\partial n_1} & \frac{\partial \mu_1}{\partial n_2} & \cdots & \frac{\partial \mu_1}{\partial n_{k-2}} & \frac{\partial \mu_1}{\partial n_{k-1}} \\ \frac{\partial \mu_2}{\partial n_1} & \frac{\partial \mu_2}{\partial n_2} & \cdots & \frac{\partial \mu_2}{\partial n_{k-2}} & \frac{\partial \mu_2}{\partial n_{k-1}} \\ \vdots & \vdots & \vdots & \vdots & \\ \frac{\partial \mu_{k-1}}{\partial n_1} & \frac{\partial \mu_{k-1}}{\partial n_2} & \cdots & \frac{\partial \mu_{k-1}}{\partial n_{k-2}} & \frac{\partial \mu_{k-1}}{\partial n_{k-1}} \end{vmatrix} \tag{21}
$$

由平衡的稳定性理论知[2-4]，式(21)右边的行列式大于0，所以问题得证.

4 结 论

任一相有温度、压力和$(k-1)$个摩尔分数共$(k+1)$个变量，其中温度和压力是各相的公共变量. 无绝热壁、刚性壁和半透壁及无化学反应、除相平衡条件约束外无其他约束的k组分和φ相$(2\leqslant\varphi\leqslant k-1)$平衡体系的独立变量个数最多为$k$，把温度和压力作为首选的独立变量，独立的浓度变量最多为$(k-2)$. 把独立的浓度变量全部选在第一相，而把其他相的浓度变量都做非独立变量. 第一相至少有一个非独立的浓度变量.

参 考 文 献

[1] Willard Gibbs J. The Collected Works of J. Willard Gibbs, Volume Ⅰ, Thermodynamics, 96

[2] Wang Zhuxi (王竹溪). Thermodynamics (Second Edition)(热力学第二版), Beijing (北京): Higher Education Press (高等教育出版社), 1983. 275, 302

[3] Zhang Shimin (张世民). Simple Discussion about Some Subjects of Physical Chemistry & Thermodynamics (物理化学和热力学若干专题浅论). Beijing (北京): Ordnance Industry Press (兵器工业出版社), 1994. 23, 68

[4] Zhang Shimin (张世民). *Chemistry* (化学), 1996, **54**: 103

[5] Zheng Chaogui (郑朝贵), Zheng Yanke (郑燕珂). *Chin. J. Chem. Phys.* (化学物理学报), 1995, **8**: 258

[6] Yuan Duqi (袁都奇). *Chin. J. Chem. Phys.* (化学物理学报), 2001, **14**: 246