

ON THE FUNDAMENTAL EQUATIONS OF THE MULTIPLE POINT

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Consider a system of $n + 2$ phases formed by means of n independent components and denote by η_i, v_i the entropy and the volume of the unit of mass of the i -th phase, and by m_{ij} the mass of the j -th component which enters into the unit of mass of the i -th phase. If we denote by $d\Pi_i/dT_i$ the slope of the pressure-temperature curve of the i -th univariant system that can be formed from the invariant system, that is to say, of the univariant system that can be formed from the invariant system by suppressing the i -th phase, then at the multiple point the following equations¹ hold :

$$\left| \begin{array}{cccccc} \frac{d\Pi_1}{dT_1}, & v_1, & m_{11}, & \dots, & m_{1n} \\ \frac{d\Pi_2}{dT_2}, & v_2, & m_{21}, & \dots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \frac{d\Pi_{n+2}}{dT_{n+2}}, & v_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n} \end{array} \right| = 0, \quad (1)$$

$$\left| \begin{array}{cccccc} \frac{dT_1}{d\Pi_1}, & \eta_1, & m_{11}, & \dots, & m_{1n} \\ \frac{dT_2}{d\Pi_2}, & \eta_2, & m_{21}, & \dots, & m_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ \frac{dT_{n+2}}{d\Pi_{n+2}}, & \eta_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n} \end{array} \right| = 0. \quad (2)$$

In a previous note² we have shown that these equations of Riecke can be written in the form

¹ Riecke. Göttinger Nachrichten, p. 223 (1890). Zeit. phys. Chem. 6, 268 (1890).

² Jour. Phys. Chem. 5, 170 (1901).

$$\sum_{i=1}^{n+2} \delta V_i \frac{d\Pi_i}{dT_i} = 0, \quad \sum_{i=1}^{n+2} \delta H_i \frac{dT_i}{d\Pi_i} = 0, \quad (3)$$

in which δV_i , δH_i denote the changes in the volume and the entropy of the i -th univariant system, corresponding to a certain reversible change of that system at the multiple point. It was shown that the reversible changes are such that

$$\sum_{i=1}^{n+2} \delta V_i = 0, \quad \sum_{i=1}^{n+2} \delta H_i = 0, \quad (4)$$

and it should have been pointed out that the $n+2$ reversible changes used in defining δV_i and δH_i constitute, when taken in succession, a reversible cycle of the invariant system. Our result can accordingly be stated as follows:

Consider at the temperature and under the pressure of the multiple point a reversible cycle of the invariant system, which can be divided into $n+2$ reversible changes, each of which involves the phases of one of the $n+2$ univariant systems. During the i -th of these reversible changes, the volume and the entropy of the invariant system receive increments δV_i , δH_i . These increments satisfy not only equations 4, but also equations 3.

Riecke's equations can be put into another form, which is even simpler than that just given.

Denote by M_i the mass of the i -th phase, by \mathfrak{M}_j the mass of the j -th component, and by H , V , the entropy and the volume of the invariant system. Then the following equations hold:

$$\begin{aligned} \sum_{i=1}^{n+2} M_i \eta_i &= H, & \sum_{i=1}^{n+2} M_i v_i &= V, \\ \sum_{i=1}^{n+2} M_i m_{ij} &= \mathfrak{M}_j, & j &= 1, 2, \dots, n. \end{aligned} \quad (5)$$

Consider at the temperature and under the pressure of the multiple point a reversible change which leaves the volume unaltered. The preceding equations give us

$$\begin{aligned}
 \sum_{i=1}^{n+2} \eta_i \delta M_i &= \delta H, & \sum_{i=1}^{n+2} v_i \delta M_i &= 0, \\
 \sum_{i=1}^{n+2} m_{ij} \delta M_i &= 0, & j &= 1, 2, \dots, n.
 \end{aligned} \quad (6)$$

From these equations 6, we obtain at once

$$\begin{vmatrix}
 \eta_1, & v_1, & m_{11}, & \dots, & m_{1n} \\
 \eta_2, & v_2, & m_{21}, & \dots, & m_{2n} \\
 \vdots & \vdots & \vdots & & \vdots \\
 \eta_{n+2}, & v_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n}
 \end{vmatrix} \delta M_i$$

$$= (-1)^{i+1} \delta H \begin{vmatrix}
 v_1, & m_{11}, & \dots, & m_{1n} \\
 \vdots & \vdots & & \vdots \\
 v_{i-1}, & m_{i-1,1}, & \dots, & m_{i-1,n} \\
 v_{i+1}, & m_{i+1,1}, & \dots, & m_{i+1,n} \\
 \vdots & \vdots & & \vdots \\
 v_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n}
 \end{vmatrix}. \quad (7)$$

The coefficient of δH in this equation is the same as the coefficient of $d\Pi_i/dT_i$ in equation 1. It follows from this without difficulty that equation 1 can be written in the form

$$\sum_{i=1}^{n+2} \delta M_i \frac{d\Pi_i}{dT_i} = 0. \quad (8)$$

Consider now at the temperature and under the pressure of the multiple point a reversible change which leaves the entropy unaltered. Equations 5 now give us

$$\begin{aligned}
 \sum_{i=1}^{n+2} v^i \delta M_i &= \delta V, & \sum_{i=1}^{n+2} \eta_i \delta M_i &= 0, \\
 \sum_{i=1}^{n+2} m_{ij} \delta M_i &= 0, & j &= 1, 2, \dots, n.
 \end{aligned} \quad (9)$$

From these we obtain at once

$$\begin{vmatrix}
 v_1, & \eta_1, & m_{11}, & \dots, & m_{1n} \\
 v_2, & \eta_2, & m_{21}, & \dots, & m_{2n} \\
 \vdots & \vdots & \vdots & & \vdots \\
 v_{n+2}, & \eta_{n+2} & m_{n+2,1}, & \dots, & m_{n+2,n}
 \end{vmatrix} \delta M_i$$

$$= (-1)^{i+1} \delta V \begin{vmatrix}
 \eta_1, & m_{11}, & \dots, & m_{1n} \\
 \vdots & \vdots & & \vdots \\
 \eta_{i-1}, & m_{i-1,1}, & \dots, & m_{i-1,n} \\
 \eta_{i+1}, & m_{i+1,1}, & \dots, & m_{i+1,n} \\
 \vdots & \vdots & & \vdots \\
 \eta_{n+2}, & m_{n+2,1}, & \dots, & m_{n+2,n}
 \end{vmatrix}. \quad (10)$$

The coefficient of δV in this equation is the same as the coefficient of $dT_i/d\Pi_i$ in equation 2. It follows that equation 2 can be written in the form

$$\sum_{i=1}^{n+2} \delta M_i \frac{dT_i}{d\Pi_i} = 0. \quad (11)$$

The fundamental equations of the multiple point can accordingly be put into the form of equations 8 and 11. It should be remembered that in the first of these equations δM_i denotes the increment of M_i due to a reversible change in which the volume is kept constant, while in the second δM_i denotes the increment of M_i due to a reversible change in which the entropy is kept constant.

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