NOTE ON THE FUNDAMENTAL EQUATIONS OF MULTIPLE POINTS

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For the $n + 2$ phases that coexist at a multiple point of an n -component system, Gibbs's theory of thermodynamic equilibrium supplies the equations,

$$-v_i dp + \eta_i d\theta + \sum_{j=1}^n m_{ij} d\mu_{ij} = 0; \quad (i = 1, 2, \dots, n + 2),$$

where

$$v_i, \quad \eta_i, \quad m_{ij}, \quad \mu_{ij}$$

denote the volume, the entropy, and the mass and chemical potential of the j -th component, of the i -th phase of the system; and p, θ the pressure and thermodynamic temperature. On eliminating the common $d\mu$'s between the successive pairs of equations, solving the resulting equations for $dp/d\theta$ and for $d\theta/dp$ respectively, and adding, we find

$$\left\{ \begin{array}{l} (\bar{v}_2 - \bar{v}_1) \frac{dp_{12}}{d\theta} + (\bar{v}_3 - \bar{v}_2) \frac{dp_{23}}{d\theta} + \dots \\ \quad + (\bar{v}_1 - \bar{v}_{n+2}) \frac{dp_{(n+2)1}}{d\theta} = 0, \quad (1) \\ (\bar{\eta}_2 - \bar{\eta}_1) \frac{d\theta_{12}}{dp} + (\bar{\eta}_3 - \bar{\eta}_2) \frac{d\theta_{23}}{dp} + \dots \\ \quad + (\bar{\eta}_1 - \bar{\eta}_{n+2}) \frac{d\theta_{(n+2)1}}{dp} = 0. \quad (2) \end{array} \right.$$

Here $\bar{v}_i$ and $\bar{\eta}_i$ denote the specific volume and the specific entropy of the i -th phase

A derivation of these so-called Fundamental Equations of the Multiple Point was given by Dr. Saurel in the March number of this Journal; and it was pointed out that, through multiplication by θ , the latter of the two is transformed to

$$\bar{Q}_{12} \frac{d\theta_{12}}{dp} + \bar{Q}_{23} \frac{d\theta_{23}}{dp} + \dots + \bar{Q}_{(n+2)1} \frac{d\theta_{(n+2)1}}{dp} = 0; \quad (2a)$$

where $\bar{Q}_{mn}$ is the heat absorbed in the transfer of unit mass from the m -th to the n -th phase at the pressure and temperature of the multiple point. To this statement should be added the complementary remark, that equation (1), through multiplication by $-\theta$, is brought into the corresponding form,

$$\bar{W}_{12} \frac{dp_{12}}{d\theta} + \bar{W}_{23} \frac{dp_{23}}{d\theta} + \dots + \bar{W}_{(n+2)1} \frac{dp_{(n+2)1}}{d\theta} = 0, \quad (1a)$$

where $\bar{W}_{mn}$ is the work absorbed in the transfer of unit mass from the m -th to the n -th phase.

It should be noted, further, that we can successively eliminate $d\theta$ and dp between the successive pairs of our initial linear equations. In the simple case of a one-component system, we find

$$\begin{vmatrix} v_1 & \eta_1 \\ v_2 & \eta_2 \end{vmatrix} \frac{dp_{12}}{d\mu} + \begin{vmatrix} v_2 & \eta_2 \\ v_3 & \eta_3 \end{vmatrix} \frac{dp_{23}}{d\mu} + \begin{vmatrix} v_3 & \eta_3 \\ v_1 & \eta_1 \end{vmatrix} \frac{dp_{31}}{d\mu} = 0, \quad (3)$$

$$\begin{vmatrix} m_1 & \eta_1 \\ m_2 & \eta_2 \end{vmatrix} \frac{d\mu_{12}}{dp} + \begin{vmatrix} m_2 & \eta_2 \\ m_3 & \eta_3 \end{vmatrix} \frac{d\mu_{23}}{dp} + \begin{vmatrix} m_3 & \eta_3 \\ m_1 & \eta_1 \end{vmatrix} \frac{d\mu_{31}}{dp} = 0, \quad (4)$$

$$\begin{vmatrix} \eta_1 & v_1 \\ \eta_2 & v_2 \end{vmatrix} \frac{d\theta_{12}}{d\mu} + \begin{vmatrix} \eta_2 & v_2 \\ \eta_3 & v_3 \end{vmatrix} \frac{d\theta_{23}}{d\mu} + \begin{vmatrix} \eta_3 & v_3 \\ \eta_1 & v_1 \end{vmatrix} \frac{d\theta_{31}}{d\mu} = 0, \quad (5)$$

$$\begin{vmatrix} m_1 & v_1 \\ m_2 & v_2 \end{vmatrix} \frac{d\mu_{12}}{d\theta} + \begin{vmatrix} m_2 & v_2 \\ m_3 & v_3 \end{vmatrix} \frac{d\mu_{23}}{d\theta} + \begin{vmatrix} m_3 & v_3 \\ m_1 & v_1 \end{vmatrix} \frac{d\mu_{31}}{d\theta} = 0, \quad (6)$$

equations which are analogous in form to the foregoing fundamental equations of the triple point.

If, now, equations (4) and (6) be multiplied through by θ and $-\theta$, respectively, they become :

$$\bar{Q}_{12} \frac{d\mu_{12}}{dp} + \bar{Q}_{23} \frac{d\mu_{23}}{dp} + \bar{Q}_{31} \frac{d\mu_{31}}{dp} = 0, \quad (4a)$$

$$\bar{W}_{12} \frac{d\mu_{12}}{d\theta} + \bar{W}_{23} \frac{d\mu_{23}}{d\theta} + \bar{W}_{31} \frac{d\mu_{31}}{d\theta} = 0, \quad (6a)$$

like equations (1a) and (2a) above. The extension of these results to n -component systems is a simple matter.

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