ON MAXWELL'S THEOREM

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The object of the present note is to give a demonstration of the theorem that the sum of the areas included between the actual and the theoretical isotherms is equal to zero, provided the areas above the actual isotherm are reckoned positive and those below negative. Originally, the theorem referred to the isotherms of a substance containing a single component, but it has been extended by Blümcke¹ to the isotherms of a substance containing two or more components, and a demonstration of the generalized theorem has recently been given by Duhem.

Consider a heterogeneous mass M , consisting of n components of masses $\mathfrak{M}_1, \mathfrak{M}_2, \dots, \mathfrak{M}_n$ and existing in the form of r homogeneous phases. If we denote the energy, entropy, volume, temperature, pressure, and masses of the components, of the i -th phase, by $E_i, H_i, V_i, t_i, p_i, M_{i1}, \dots, M_{in}$ (so that M_{ij} denotes the mass of the j -th component in the i -th phase), we shall have the relation²

$$dE_i = t_i dH_i - p_i dV_i + \lambda_{i1} dM_{i1} + \lambda_{i2} dM_{i2} + \dots + \lambda_{in} dM_{in}. \quad (1)$$

In order that the various phases should coexist it is necessary³ that

$$\begin{aligned} t_1 &= t_2 = \dots = t_r = t \\ p_1 &= p_2 = \dots = p_r = p \\ \lambda_{11} &= \lambda_{21} = \dots = \lambda_{r1} = \lambda_1 \\ \lambda_{12} &= \lambda_{22} = \dots = \lambda_{r2} = \lambda_2 \\ &\dots \\ \lambda_{1n} &= \lambda_{2n} = \dots = \lambda_{rn} = \lambda_n. \end{aligned}$$

¹ Blümcke. Zeit. phys. Chem. **6**, 153 (1890).

² Gibbs. On the Equilibrium of Heterogeneous Substances, p. 116.

³ Gibbs. Ibid. p. 119.

Taking the sum of the r equations of the form (1), and writing

$$\begin{aligned} E &= \Sigma E_i, & H &= \Sigma H_i, & V &= \Sigma V_i, \\ \mathfrak{M}_1 &= \Sigma M_{i1}, & \mathfrak{M}_2 &= \Sigma M_{i2}, & \dots, & \mathfrak{M}_n = \Sigma M_{in}, \end{aligned}$$

we shall have, for the whole mass,

$$dE = t dH - p dV + \lambda_1 d\mathfrak{M}_1 + \lambda_2 d\mathfrak{M}_2 + \dots + \lambda_n d\mathfrak{M}_n. \quad (2)$$

Moreover, as the energy is a homogeneous function of the first degree of the entropy, volume, and masses of the components, we have

$$E = tH - pV + \lambda_1 \mathfrak{M}_1 + \lambda_2 \mathfrak{M}_2 + \dots + \lambda_n \mathfrak{M}_n. \quad (3)$$

If we write

$$\epsilon = \frac{E}{M}, \quad \eta = \frac{H}{M}, \quad v = \frac{V}{M}, \quad c_1 = \frac{\mathfrak{M}_1}{M}, \quad c_2 = \frac{\mathfrak{M}_2}{M}, \quad \dots, \quad c_n = \frac{\mathfrak{M}_n}{M},$$

equations (2) and (3) become

$$\begin{aligned} M d\epsilon + \epsilon dM &= M (t d\eta - p dv + \lambda_1 dc_1 + \lambda_2 dc_2 + \dots + \lambda_n dc_n) \\ &\quad + (t\eta - pv + \lambda_1 c_1 + \lambda_2 c_2 + \dots + \lambda_n c_n) dM, \\ \epsilon &= t\eta - pv + \lambda_1 c_1 + \lambda_2 c_2 + \dots + \lambda_n c_n, \end{aligned}$$

and consequently

$$d\epsilon = t d\eta - p dv + \lambda_1 dc_1 + \lambda_2 dc_2 + \dots + \lambda_n dc_n. \quad (4)$$

This equation connects the changes in the average energy, entropy, volume and concentrations during any actual change in the system.

On the other hand, if we denote the energy, entropy, volume, temperature, pressure, and masses of the components, of the unit of mass of the i th phase, by ϵ_i , η_i , v_i , t_i , p_i , m_{i1} , m_{i2} , $\dots$, m_{in} , the reasoning which served to establish equation (1) will also serve to establish the equation

$$d\epsilon_i = t_i d\eta_i - p_i dv_i + \mu_{i1} dm_{i1} + \mu_{i2} dm_{i2} + \dots + \mu_{in} dm_{in}. \quad (5)$$

ϵ_i is thus a function of η_i , v_i , m_{i1} , m_{i2} , $\dots$, m_{in} ; and we shall assume that the functions obtained in this manner for the various phases are not distinct functions but are parts of one and the same uniform analytical function. If, then, the system undergoes a transformation by which it passes from one homogeneous

phase to a second homogeneous phase, we may calculate the change in the energy either by equation (4) or by equation (5). If, in particular, we suppose the transformation to take place at constant temperature and with constant concentrations, we shall have from equation (4),

$$\epsilon_2 - \epsilon_1 = t(\eta_2 - \eta_1) - \int_1^2 p dv,$$

and from equation (5)

$$\epsilon_2 - \epsilon_1 = t(\eta_2 - \eta_1) - \int_1^2 p_i dv_i.$$

A comparison of these equations yields

$$\int_1^2 p dv = \int_1^2 p_i dv_i;$$

and since p and v are the pressure and volume along the actual isotherm, and p_i and v_i are the pressure and volume along the theoretical isotherm, the theorem is demonstrated.

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