

# ON THE DEMONSTRATION OF THE PHASE RULE<sup>1</sup>

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If the energy, entropy, volume, temperature, pressure, and masses of the components of a phase be denoted by  $\epsilon$ ,  $\eta$ ,  $v$ ,  $t$ ,  $p$ ,  $m_1$ ,  $m_2$ , ...,  $m_n$ , it can be shown that

$$d\epsilon = t d\eta - p dv + \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_n dm_n.$$

If it be admitted that  $\epsilon$  is a function of the independent variables  $\eta$ ,  $v$ ,  $m_1$ ,  $m_2$ , ...,  $m_n$ , it follows that  $t$ ,  $-p$ ,  $\mu_1$ ,  $\mu_2$ , ...,  $\mu_n$  are the first derivatives of  $\epsilon$ . Moreover,  $\epsilon$  is a homogeneous function of the first degree of  $\eta$ ,  $v$ ,  $m_1$ ,  $m_2$ , ...,  $m_n$ ; for, when the entropy, volume, and masses are increased  $k$ -fold, the energy is also increased  $k$ -fold. Accordingly, by Euler's theorem,

$$\epsilon = t\eta - pv + \mu_1 m_1 + \mu_2 m_2 + \dots + \mu_n m_n.$$

The comparison of these two equations yields the equation:

$$0 = \eta dt - v dp + m_1 d\mu_1 + m_2 d\mu_2 + \dots + m_n d\mu_n;$$

and from this equation Gibbs<sup>2</sup> concludes that there exists an integral relation between  $p$ ,  $t$ ,  $\mu_1$ ,  $\mu_2$ , ...,  $\mu_n$ . This conclusion is unwarranted; but it is nevertheless correct, as may be shown by the following reasoning.  $\epsilon$  is a homogeneous function of the first degree of  $\eta$ ,  $v$ ,  $m_1$ ,  $m_2$ , ...,  $m_n$ ; its derivatives,  $t$ ,  $-p$ ,  $\mu_1$ ,  $\mu_2$ , ...,  $\mu_n$ , are therefore homogeneous functions of the degree zero, that is to say they are functions of the ratios  $\frac{\eta}{v}$ ,  $\frac{m_1}{v}$ ,  $\frac{m_2}{v}$ , ...,  $\frac{m_n}{v}$ . If, then, from the  $n + 2$  equations which define  $t$ ,  $-p$ ,

$\mu_1$ ,  $\mu_2$ , ...,  $\mu_n$  in terms of  $\eta$ ,  $v$ ,  $m_1$ ,  $m_2$ , ...,  $m_n$ , we eliminate the  $n + 1$  ratios  $\frac{\eta}{v}$ ,  $\frac{m_1}{v}$ ,  $\frac{m_2}{v}$ , ...,  $\frac{m_n}{v}$ , we shall find an integral rela-

<sup>1</sup> This note has already appeared, in part, in the *Procès-verbaux des Séances de la Société des Sciences de Bordeaux*.

<sup>2</sup> Gibbs. On the Equilibrium of Homogeneous Substances, p. 143.

tion between  $p, t, \mu_1, \mu_2, \dots, \mu_n$ . The existence of this relation is an essential point in Gibbs's demonstration of the phase rule. The existence of the relation between  $p, t, \mu_1, \mu_2, \dots, \mu_n$  can also be established by means of the following theorem:

If  $X_1, X_2, \dots, X_n$  are the first derivatives of a function  $F$  of the independent variables  $x_1, x_2, \dots, x_n$ , so that

$$dF = X_1 dx_1 + X_2 dx_2 + \dots + X_n dx_n;$$

and if, further,  $F$  be such that

$$F = X_1 x_1 + X_2 x_2 + \dots + X_n x_n,$$

then the functions  $X_1, X_2, \dots, X_n$  are not independent, but are connected by an integral equation.

For, the comparison of the two above equations yields the third:

$$x_1 dX_1 + x_2 dX_2 + \dots + x_n dX_n = 0;$$

or, as it may be written:

$$\begin{aligned} & \left[ x_1 \frac{\partial X_1}{\partial x_1} + x_2 \frac{\partial X_2}{\partial x_1} + \dots + x_n \frac{\partial X_n}{\partial x_1} \right] dx_1 \\ & + \left[ x_1 \frac{\partial X_1}{\partial x_2} + x_2 \frac{\partial X_2}{\partial x_2} + \dots + x_n \frac{\partial X_n}{\partial x_2} \right] dx_2 \\ & \quad \vdots \quad \quad \quad \vdots \\ & + \left[ x_1 \frac{\partial X_1}{\partial x_n} + x_2 \frac{\partial X_2}{\partial x_n} + \dots + x_n \frac{\partial X_n}{\partial x_n} \right] dx_n = 0. \end{aligned}$$

As the differentials  $dx_1, dx_2, \dots, dx_n$  are independent, this equation requires that the coefficients of these differentials should be equal to zero; and the elimination of  $x_1, x_2, \dots, x_n$  from the  $n$  resulting equations yields:

$$\begin{vmatrix} \frac{\partial X_1}{\partial x_1} & \frac{\partial X_2}{\partial x_1} & \dots & \frac{\partial X_n}{\partial x_1} \\ \frac{\partial X_1}{\partial x_2} & \frac{\partial X_2}{\partial x_2} & \dots & \frac{\partial X_n}{\partial x_2} \\ \vdots & \vdots & & \vdots \\ \frac{\partial X_1}{\partial x_n} & \frac{\partial X_2}{\partial x_n} & \dots & \frac{\partial X_n}{\partial x_n} \end{vmatrix} = 0.$$

The vanishing of the Jacobian of  $X_1, X_2, \dots, X_n$  shows that these functions are not independent but are connected by an integral equation.

The application of this theorem to the functions  $t, -p, \mu_1, \mu_2, \dots, \mu_n$  which satisfy the equations :

$$\begin{aligned} d\epsilon &= td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_n dm_n, \\ \epsilon &= t\eta - pv + \mu_1 m_1 + \mu_2 m_2 + \dots + \mu_n m_n \end{aligned}$$

is evident.

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