[AMERICAN JOURNAL OF SCIENCE, VOL. 255, APRIL 1957, P. 261-265]

EVALUATION OF THE CHEMICAL POTENTIAL IN TERMS OF INTENSIVE QUANTITIES

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ABSTRACT. The chemical potential was defined by J. Willard Gibbs in terms of extensive quantities. That it is nevertheless an intensive quantity therefore requires proof. In this paper an elementary proof is given that results in an explicit evaluation of the chemical potential in terms of intensive quantities:

$$\mu_k = E - TS + pV - m_1\left(\frac{\partial E}{\partial m_1}\right)_{SVm_2 \ldots m_{n-1}} - \ldots$$

$$+ (1-m_k)\left(\frac{\partial E}{\partial m_k}\right)_{SVm_1 \ldots m_{k-1}m_{k+1} \ldots m_{n-1}}$$

$$- \ldots - m_{n-1}\left(\frac{\partial E}{\partial m_{n-1}}\right)_{SVm_1 \ldots m_{n-2}},$$

where μ_k denotes the chemical potential, E denotes the specific energy, T denotes the absolute temperature, S denotes the specific entropy, p denotes the pressure, V denotes the specific volume, and m_k denotes the mass fraction of component k.

Since the chemical potential is thus shown to be equal to a function of intensive quantities only it is itself an intensive quantity.

The chemical potential, which was introduced by J. Willard Gibbs (1876, p. 116, 144) is the cornerstone of chemical thermodynamics, and the phase rule, which has come to play such an important role in studies of mineral and rock formation as well as in chemical and metallurgical researches, is a corollary of the quantitative relations of the chemical potentials in phases at equilibrium established by him.

The chemical potential μ_k of a phase made up of n components with respect to the kth component was defined by Gibbs (1876, p. 116, 144) by the equation

$$\mu_k = \left(\frac{\partial \mathbf{E}}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n}, \qquad (1)$$

where $\mathbf{E}$ denotes the total energy of the phase, $\mathbf{S}$ denotes its total entropy, $\mathbf{V}$ denotes its total volume, $\mathbf{m}_1$ denotes the mass of component 1 in the phase, $\mathbf{m}_2$ the mass of component 2, $\mathbf{m}_k$ the mass of component k and $\mathbf{m}_n$ the mass of component n. Gibbs (1876, p. 144) stated that the chemical potential is "independent of the quantity of the mass considered" and proofs that a partial quantity such as the chemical potential depends only on the temperature, pressure, and composition have been given by Butler (1936, p. 89, 90), by Keenan (1941, p. 231), and by Glasstone (1947, p. 215).[1] An elementary proof that the chemical potential depends only on intensive quantities is pre-

[1] The derivation given by Butler (1936) and by Glasstone (1947) was carried out by the application of Euler's theorem on homogeneous functions and is elegant and brief. Euler's theorem was itself proved by means of the chain rule for differentiation of a function of a function. The proof given in this paper, which makes use only of the chain rule for differentiation of a function of a function, is thus more elementary. Almost all petrologists and physical chemists have studied the chain rule for differentiation of a function of a function, but not all have studied Euler's theorem on homogeneous functions and the more elementary proof is of value particularly to the latter.

sented in this paper. This proof is accomplished by the use of the standard equation for change of variables in partial differentiation and it results in an explicit evaluation of the chemical potential in terms of functions involving only quantities that are intensive by definition. The resulting equation may or may not be found of direct practical use. It is presented chiefly for its value in showing clearly that the chemical potential depends only on intensive quantities and is therefore itself an intensive quantity.

The evaluation of the chemical potential in terms of intensive quantities is carried out by the following method. The specific energy E of the phase is defined as the total energy $\mathbf{E}$ divided by the total mass $\mathbf{M}$,

$$E = \frac{\mathbf{E}}{\mathbf{M}}, \tag{2}$$

and the total mass $\mathbf{M}$ is of course equal to the sum of the masses of the n components

$$\mathbf{M} = \mathbf{m}_1 + \ldots + \mathbf{m}_n . \tag{3}$$

Thus

$$\begin{aligned} \mu_k &= \left(\frac{\partial \mathbf{M}E}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n} \\ &= \mathbf{M}\left(\frac{\partial E}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n} + E . \end{aligned} \tag{4}$$

The specific energy E is a function of the specific entropy S, the specific volume V, and the mass fractions $m_1, m_2, \ldots m_{n-1}$, which are defined by the equations $S = \mathbf{S/M}$, $V = \mathbf{V/M}$, $m_1 = \mathbf{m}_1/\mathbf{M}$, $m_2 = \mathbf{m}_2/\mathbf{M}$, $\cdots$, $m_{n-1} = \mathbf{m}_{n-1}/\mathbf{M}$ respectively. Application of the theorem for change of variables in partial differentiation therefore gives the equation

$$\begin{aligned} &\left(\frac{\partial E}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n} = \\ &\left(\frac{\partial E}{\partial S}\right)_{Vm_1 \ldots m_{n-1}} \left(\frac{\partial S}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n} \\ &+ \left(\frac{\partial E}{\partial V}\right)_{Sm_1 \ldots m_{n-1}} \left(\frac{\partial V}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n} \\ &+ \left(\frac{\partial E}{\partial m_1}\right)_{SVm_2 \ldots m_{n-1}} \left(\frac{\partial m_1}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \cdots \mathbf{m}_n} + \ldots + \\ &\left(\frac{\partial E}{\partial m_k}\right)_{SVm_1 \ldots m_{k-1}m_{k+1} \ldots m_{n-1}} \left(\frac{\partial m_k}{\partial \mathbf{m}_k}\right) \mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n \\ &+ \ldots + \left(\frac{\partial E}{\partial m_{n-1}}\right)_{SVm_1 \ldots m_{n-2}} \left(\frac{\partial m_{n-1}}{\partial \mathbf{m}_k}\right) \mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n . \end{aligned} \tag{5}$$

The partial derivative $\left(\frac{\partial S}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n}$ can also be evaluated by application of the theorem for change of variables. Thus one has

$$\left(\frac{\partial S}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n}$$
$$= \mathbf{S}\left(\frac{\partial \mathbf{M}^{-1}}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n}$$
$$= -\frac{\mathbf{S}}{\mathbf{M}^2} = -\frac{S}{\mathbf{M}} \cdot \tag{6}$$

Likewise one has

$$\left(\frac{\partial V}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n}$$
$$= \mathbf{V}\left(\frac{\partial \mathbf{M}^{-1}}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n}$$
$$= -\frac{\mathbf{V}}{\mathbf{M}^2} = -\frac{V}{\mathbf{M}} , \tag{7}$$

also

$$\left(\frac{\partial m_1}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n}$$
$$= \mathbf{m}_1\left(\frac{\partial \mathbf{M}^{-1}}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n}$$
$$= -\frac{\mathbf{m}_1}{\mathbf{M}^2}$$
$$= -\frac{m_1}{\mathbf{M}} , \tag{8}$$

and

$$\left(\frac{\partial m_k}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n}$$
$$= \mathbf{m}_k\left(\frac{\partial \mathbf{M}^{-1}}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n} + \frac{1}{\mathbf{M}}$$
$$= -\frac{\mathbf{m}_k}{\mathbf{M}^2} + \frac{1}{\mathbf{M}}$$
$$= \frac{1 - m_k}{\mathbf{M}} , \tag{9}$$

and

$$\left(\frac{\partial m_{n-1}}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n}$$
$$= \mathbf{m}_{n-1}\left(\frac{\partial \mathbf{M}^{-1}}{\partial \mathbf{m}_k}\right)_{\mathbf{SVm}_1 \ldots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \ldots \mathbf{m}_n}$$
$$= -\frac{\mathbf{m}_{n-1}}{\mathbf{M}^2}$$
$$= -\frac{m_{n-1}}{\mathbf{M}} . \tag{10}$$

Substituting in equation (4) the values of the partial derivatives in equations (5), (6), (7), (8), (9), and (10) one obtains the result

$$\mu_k = E - S\left(\frac{\partial E}{\partial S}\right)_{Vm_1 \ldots m_{n-1}} - V\left(\frac{\partial E}{\partial V}\right)_{Sm_1 \ldots m_{n-1}}$$
$$- m_1\left(\frac{\partial E}{\partial m_1}\right)_{SVm_2 \ldots m_{n-1}} - \ldots$$
$$+ (1-m_k)\left(\frac{\partial E}{\partial m_k}\right)_{SVm_1 \ldots m_{k-1}m_{k+1} \ldots m_{n-1}}$$
$$- \ldots - m_{n-1}\left(\frac{\partial E}{\partial m_{n-1}}\right)_{SVm_1 \ldots m_{n-2}} . \qquad (11)$$

The values of the partial derivatives $\left(\frac{\partial E}{\partial S}\right)_{Vm_1 \ldots m_{n-1}}$ and $\left(\frac{\partial E}{\partial V}\right)_{Sm_1 \ldots m_{n-1}}$ are the same as the values of the partial derivatives of the energy of a one-component one-phase system of constant mass with respect to the entropy and with respect to the volume,[2] that is,

$$\left(\frac{\partial E}{\partial S}\right)_{Vm_1 \ldots m_{n-1}} = T \quad , \qquad (12)$$

and

$$\left(\frac{\partial E}{\partial V}\right)_{Sm_1 \ldots m_{n-1}} = -p . \qquad (13)$$

Hence one has finally

$$\mu_k = E - TS + pV - m_1\left(\frac{\partial E}{\partial m_1}\right)_{SVm_2 \ldots m_{n-1}} - \ldots$$
$$+ (1-m_k)\left(\frac{\partial E}{\partial m_k}\right)_{SVm_1 \ldots m_{k-1}m_{k+1} \ldots m_{n-1}} - \ldots$$
$$- m_{n-1}\left(\frac{\partial E}{\partial m_{n-1}}\right)_{SVm_1 \ldots m_{n-2}} .[3] \qquad (14)$$

This equation expresses the chemical potential explicitly in terms of intensive quantities.

$$\mu_k = \left(\frac{\partial \mathbf{G}}{\partial \mathbf{m}_k}\right)_{\mathbf{Tpm}_1 \cdots \mathbf{m}_{k-1}\mathbf{m}_{k+1} \cdots \mathbf{m}_n} ,$$

but for the purposes of this paper it seemed best to start with Gibbs' original definition.

In the special case of a phase made up of two components, the two chemical potentials can thus be expressed by the equations

[2] The values of the partial derivatives of the energy of a one-component one-phase system of constant mass with respect to the entropy and with respect to the volume are given by Bridgman (1925, p. 11, 12).

[3] The chemical potential can be evaluated in terms of intensive quantities more briefly by starting with the equation

$$\mu_1 = E - TS + pV + m_2\left(\frac{\partial E}{\partial m_1}\right)_{SV} \tag{15}$$

and

$$\mu_2 = E - TS + pV - m_1\left(\frac{\partial E}{\partial m_1}\right)_{SV} . \tag{16}$$

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