LETTERS TO THE EDITORS

PHYSICS

Thermodynamical Relations in Two-Component Two-Phase Systems

GIBBS¹, in his discussion of the phase rule, arrives at certain relations among the pressure, temperature and chemical potentials for two-component two-phase systems, making use of a fundamental equation now commonly known as the Gibbs–Duhem relation. A detailed account of this work has been given by Butler². Since these systems have two degrees of freedom, the derivatives involving the intensive variables are of the form $(\partial x/\partial y)_z$. By introducing second-order Jacobians, the properties of the systems in question can be summarized compactly, and the results given by Gibbs and Butler readily obtained. The first systematic application of Jacobians to thermodynamical systems was made by Shaw³. The chief property required here is that:

$$(\partial x/\partial y)_z = J(x, z)/J(y, z)$$

where

$$J(x, z) = \begin{vmatrix} (\partial x/\partial \beta)_\gamma & (\partial x/\partial \gamma)_\beta \\ (\partial z/\partial \beta)_\gamma & (\partial z/\partial \gamma)_\beta \end{vmatrix}$$

β and γ being any two admissible variables.

The Gibbs–Duhem equations for a two-component two-phase system are:

$$S^{(i)}dT - v^{(i)}dp + m_1^{(i)}d\mu_1 + m_2^{(i)}d\mu_2 = 0 \quad (i = 1, 2) \quad (1)$$

where superscripts are used to distinguish the phases.

In Jacobian notation:

$$S^{(i)}J(T, x) - v^{(i)}J(p, x) + m_1^{(i)}J(\mu_1, x) + m_2^{(i)}J(\mu_2, x) = 0 \quad (i = 1, 2) \quad (2)$$

On setting $x = p, T, \mu_1, \mu_2$, in turn, sets of homogeneous equations of the following form are obtained:

$$\begin{aligned} a_1y + b_1z + c_1w &= 0 \\ a_2y + b_2z + c_2w &= 0 \end{aligned}$$

leading to the ratios:

$$\frac{y}{\begin{vmatrix} b_1 & c_1 \\ b_2 & c_2 \end{vmatrix}} = \frac{z}{\begin{vmatrix} c_1 & a_1 \\ c_2 & a_2 \end{vmatrix}} = \frac{w}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}$$

Writing

$$\begin{aligned} M &= \begin{vmatrix} m_1^{(1)} & m_2^{(1)} \\ m_1^{(2)} & m_2^{(2)} \end{vmatrix} & W &= \begin{vmatrix} v^{(1)} & S^{(1)} \\ v^{(2)} & S^{(2)} \end{vmatrix} \\ S_1 &= \begin{vmatrix} S^{(1)} & m_1^{(1)} \\ S^{(2)} & m_1^{(2)} \end{vmatrix} & S_2 &= \begin{vmatrix} S^{(1)} & m_2^{(1)} \\ S^{(2)} & m_2^{(2)} \end{vmatrix} \\ V_1 &= \begin{vmatrix} v^{(1)} & m_1^{(1)} \\ v^{(2)} & m_1^{(2)} \end{vmatrix} & V_2 &= \begin{vmatrix} v^{(1)} & m_2^{(1)} \\ v^{(2)} & m_2^{(2)} \end{vmatrix} \end{aligned}$$

and setting $J(p, T) = M\alpha$, we obtain the Jacobians given in Table 1. The Jacobian $J(x, y)$ is found at the intersection of the row labelled x and the column labelled y .

Applications. If $m_1^{(1)} = km_1^{(2)}$, and $m_2^{(1)} = km_2^{(2)}$, then $M = 0$, so that:

$$\begin{aligned} (\partial p/\partial \mu_1)_T &= J(p, T)/J(\mu_1, T) = M/V_2 = 0 \\ (\partial T/\partial \mu_1)_p &= J(T, p)/J(\mu_1, p) = -M/S_2 = 0 \end{aligned}$$

Table 1. TABLE OF JACOBIANS

$x \rightarrow y$	p	T	μ_1	μ_2
p	0	$M\alpha$	$-S_2\alpha$	$S_1\alpha$
T	$-M\alpha$	0	$-V_2\alpha$	$V_1\alpha$
μ_1	$S_2\alpha$	$V_2\alpha$	0	$-W\alpha$
μ_2	$-S_1\alpha$	$-V_1\alpha$	$W\alpha$	0

that is, if the composition of the phases is identical, then, at constant temperature, the pressure is in general a maximum or a minimum, and at constant pressure, the temperature is in general a maximum or a minimum (Gibbs–Konowalov laws).

Again, $M = 0$ implies $J(p, T) = 0$; that is, there is a functional relation between p and T , $p = f(T)$. Hence, $dp/dT = (\partial p/\partial T)_{\mu_1} = S_2/V_2$, the same relation as for a one-component two-phase system (essentially the Clausius–Clapeyron equation).

H. KAUFMAN

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¹ Gibbs, J. W., "Collected Works", 1, 99 (1928).

² Butler, J. A. V., "Commentary on the Scientific Writings of J. Willard Gibbs", 1, 111 (1936).

³ Shaw, A. N., *Phil. Trans. Roy. Soc., A*, 234, 299 (1935).

Cosmic Ray Intensity in Interplanetary Space

THE primary cosmic ray intensity at the Earth shows characteristic variations in time which are related to solar and geomagnetic activity. This relationship exists partly because of the modulation of the galactic cosmic ray flux by interplanetary magnetic and electric fields and partly because of the acceleration of particles to cosmic ray energies on or near the Sun. The eleven-year variation, the sharp drop in intensity associated with great magnetic storms, the quasi-periodic 27-day variation and the solar daily variation appear to belong to the former category. The occasional very large, and more frequent small increases in intensity, associated with solar flares are due to local production of high-energy particles. Detailed study of these variations in intensity has led to the development of several alternative models of the interplanetary magnetic field.

According to one of these models¹, the cosmic ray time variations can be explained in terms of a rather regular interplanetary magnetic field generated by current systems flowing in the solar corona and having a high degree of axial symmetry. This field would therefore be predominantly dipolar, and in order to explain the observed cosmic ray intensity variations it would need to have a strength of 10^{-5} – 10^{-4} gauss near the Earth's orbit. The actual value would depend on the level of solar activity, the high value corresponding to sunspot maximum and the low value to sunspot minimum. It is further supposed in this model that the field contains small-scale