APPENDIX A

SOME RELATIONS INVOLVING PARTIAL DERIVATIVES

A-1 PARTIAL DERIVATIVES

In thermodynamics we are interested in continuous functions of three (or more) variables

$$\psi = \psi(x, y, z) \tag{A.1}$$

If two independent variables, say y and z, are held constant, ψ becomes a function of only one independent variable x, and the derivative of ψ with respect to x may be defined and computed in the standard fashion. The derivative so obtained is called the *partial derivative* of ψ with respect to x and is denoted by the symbol $(\partial\psi/\partial x)_{y,z}$ or simply by $\partial\psi/\partial x$. The derivative depends upon x and upon the values at which y and z are held during the differentiation; that is $\partial\psi/\partial x$ is a function of x, y, and z. The derivatives $\partial\psi/\partial y$ and $\partial\psi/\partial z$ are defined in an identical manner.

The function $\partial\psi/\partial x$, if continuous, may itself be differentiated to yield three derivatives which are called the *second partial derivatives* of ψ

$$\frac{\partial}{\partial x}\left(\frac{\partial\psi}{\partial x}\right) \equiv \frac{\partial^2\psi}{\partial x^2}$$

$$\frac{\partial}{\partial y}\left(\frac{\partial\psi}{\partial x}\right) \equiv \frac{\partial^2\psi}{\partial y\,\partial x} \tag{A.2}$$

$$\frac{\partial}{\partial z}\left(\frac{\partial\psi}{\partial x}\right) \equiv \frac{\partial^2\psi}{\partial z\,\partial x}$$

By partial differentiation of the functions $\partial\psi/\partial y$ and $\partial\psi/\partial z$, we obtain other second partial derivatives of ψ

$$\frac{\partial^2\psi}{\partial x\,\partial y} \qquad \frac{\partial^2\psi}{\partial y^2} \qquad \frac{\partial^2\psi}{\partial z\,\partial y} \qquad \frac{\partial^2\psi}{\partial x\,\partial z} \qquad \frac{\partial^2\psi}{\partial y\,\partial z} \qquad \frac{\partial^2\psi}{\partial z^2}$$

It may be shown that under the continuity conditions that we have assumed for and its partial derivatives the order of differentiation is immaterial, so that

$$\frac{\partial^2\psi}{\partial x\,\partial y} = \frac{\partial^2\psi}{\partial y\,\partial x}, \qquad \frac{\partial^2\psi}{\partial x\,\partial z} = \frac{\partial^2\psi}{\partial z\,\partial x}, \qquad \frac{\partial^2\psi}{\partial y\,\partial z} = \frac{\partial^2\psi}{\partial z\,\partial y} \qquad (A.3)$$

There are therefore just six nonequivalent second partial derivatives of a function of three independent variables (three for a function of two variables, and $\frac{1}{2}n(n+1)$ for a function of n variables).

A-2 TAYLOR'S EXPANSION

The relationship between $\psi(x, y, z)$ and $\psi(x + dx, y + dy, z + dz)$, where dx, dy, and dz denote arbitrary increments in x, y, and z, is given by Taylor's expansion

$$\psi(x+dx, y+dy, z+dz)$$
$$= \psi(x, y, z) + \left(\frac{\partial\psi}{\partial x}dx + \frac{\partial\psi}{\partial y}dy + \frac{\partial\psi}{\partial z}dz\right) + \frac{1}{2}\left[\frac{\partial^2\psi}{\partial x^2}(dx)^2 + \frac{\partial^2\psi}{\partial y^2}(dy)^2 + \frac{\partial^2\psi}{\partial z^2}(dz)^2 + 2\frac{\partial^2\psi}{\partial x\,\partial y}dx\,dy + 2\frac{\partial^2\psi}{\partial x\,\partial z}dx\,dz + 2\frac{\partial^2\psi}{\partial y\,\partial z}dy\,dz\right] + \cdots \qquad (A.4)$$

This expansion can be written in a convenient symbolic form

$$\psi(x + dx, y + dy, z + dz) = e^{(dx(\partial/\partial x) + dy(\partial/\partial y) + dz(\partial/\partial z))}\psi(x, y, z) \qquad (A.5)$$

Expansion of the symbolic exponential according to the usual series

$$e^x = 1 + x + \frac{1}{2!}x^2 + \cdots + \frac{1}{n!}x^n + \cdots \qquad (A.6)$$

then reproduces the Taylor expansion (equation A.4)

DIFFERENTIALS

The Taylor expansion (equation A.4) can also be written in the form

$$\psi(x + dx, y + dy, z + dz) - \psi(x, y, z) = d\psi + \frac{1}{2!}d^2\psi + \cdots + \frac{1}{n!}d^n\psi \cdots \qquad (A.7)$$

where

$$d\psi \equiv \frac{\partial\psi}{\partial x}dx + \frac{\partial\psi}{\partial y}dy + \frac{\partial\psi}{\partial z}dz \qquad (A.8)$$

$$d^2\psi = \frac{\partial^2\psi}{\partial x^2}(dx)^2 + \frac{\partial^2\psi}{\partial y^2}(dy)^2 + \frac{\partial^2\psi}{\partial z^2}(dz)^2 + 2\frac{\partial^2\psi}{\partial x\,\partial y}dx\,dy + 2\frac{\partial^2\psi}{\partial x\,\partial z}dx\,dz + 2\frac{\partial^2\psi}{\partial y\,\partial z}dy\,dz \qquad (A.9)$$

and generally

$$d^n\psi = \left(dx\frac{\partial}{\partial x} + dy\frac{\partial}{\partial y} + dz\frac{\partial}{\partial z}\right)^n\psi(x, y, z) \qquad (A.10)$$

These quantities $d\psi, d^2\psi, \ldots, d^n\psi, \ldots$ are called the *first-*, *second-*, and *nth-order differentials* of ψ.

A-4 COMPOSITE FUNCTIONS

Returning to the first-order differential

$$d\psi = \left(\frac{\partial\psi}{\partial x}\right)_{y,z}dx + \left(\frac{\partial\psi}{\partial y}\right)_{x,z}dy + \left(\frac{\partial\psi}{\partial z}\right)_{x,y}dz \qquad (A.11)$$

an interesting case arises when x, y, and z are not varied independently but are themselves considered to be functions of some variable u. Then

$$dx = \frac{dx}{du}du \qquad dy = \frac{dy}{du}du \qquad \text{and} \qquad dz = \frac{dz}{du}du$$

whence

$$d\psi = \left[\left(\frac{\partial\psi}{\partial x}\right)_{y,z}\frac{dx}{du} + \left(\frac{\partial\psi}{\partial y}\right)_{x,z}\frac{dy}{du} + \left(\frac{\partial\psi}{\partial z}\right)_{x,y}\frac{dz}{du}\right]du \qquad (A.12)$$

or

$$\frac{d\psi}{du} = \left(\frac{\partial \psi}{\partial x}\right)_{y,z} \frac{dx}{du} + \left(\frac{\partial \psi}{\partial y}\right)_{x,z} \frac{dy}{du} + \left(\frac{\partial \psi}{\partial z}\right)_{x,y} \frac{dz}{du} \tag{A.13}$$

If x and y are functions of two (or more) variables, say u and v, then

$$dx = \left(\frac{\partial x}{\partial u}\right)_v du + \left(\frac{\partial x}{\partial v}\right)_u dv, \qquad \text{etc.}$$

and

$$d\psi = \left[\left(\frac{\partial \psi}{\partial x}\right)_{y,z}\left(\frac{\partial x}{\partial u}\right)_v + \left(\frac{\partial \psi}{\partial y}\right)_{x,z}\left(\frac{\partial y}{\partial u}\right)_v + \left(\frac{\partial \psi}{\partial u}\right)_{x,y}\left(\frac{\partial z}{\partial u}\right)_v\right] du$$
$$+ \left[\left(\frac{\partial \psi}{\partial x}\right)_{y,z}\left(\frac{\partial x}{\partial v}\right)_u + \left(\frac{\partial \psi}{\partial y}\right)_{x,z}\left(\frac{\partial y}{\partial v}\right)_u + \left(\frac{\partial \psi}{\partial z}\right)_{x,y}\left(\frac{\partial z}{\partial v}\right)_u\right] dv \tag{A.14}$$

or

$$d\psi = \left(\frac{\partial \psi}{\partial u}\right)_v du + \left(\frac{\partial \psi}{\partial v}\right)_u dv \tag{A.15}$$

where

$$\left(\frac{\partial \psi}{\partial u}\right)_v = \left(\frac{\partial \psi}{\partial x}\right)_{y,z}\left(\frac{\partial x}{\partial u}\right)_v + \left(\frac{\partial \psi}{\partial y}\right)_{x,z}\left(\frac{\partial y}{\partial u}\right)_v + \left(\frac{\partial \psi}{\partial z}\right)_{x,y}\left(\frac{\partial z}{\partial u}\right)_v \tag{A.16}$$

and similarly for $(\partial\psi/\partial v)_u$.

It may happen that u is identical to x itself. Then

$$\left(\frac{\partial \psi}{\partial x}\right)_v = \left(\frac{\partial \psi}{\partial x}\right)_{y,z} + \left(\frac{\partial \psi}{\partial y}\right)_{x,z}\left(\frac{\partial y}{\partial x}\right)_v + \left(\frac{\partial \psi}{\partial z}\right)_{x,y}\left(\frac{\partial z}{\partial x}\right)_v \tag{A.17}$$

Other special cases can be treated similarly.

A-5 IMPLICIT FUNCTIONS

If ψ is held constant, the variations of x, y, and z are not independent, and the relation

$$\psi(x, y, z) = \text{constant} \tag{A.18}$$

es an implicit functional relation among x, y, and z. This relation may be solved for one variable, say z, in terms of the other two

$$z = z(x, y) \tag{A.19}$$

This function can then be treated by the techniques previously described to derive certain relations among the partial derivatives. However, a more direct method of obtaining the appropriate relations among the partial derivatives is merely to put $d\psi = 0$ in equation A.8.

$$0 = \left(\frac{\partial \psi}{\partial x}\right)_{y,z} dx + \left(\frac{\partial \psi}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \psi}{\partial z}\right)_{x,y} dz \tag{A.20}$$

If we now put $dz = 0$ and divide through by dx, we find

$$0 = \left(\frac{\partial \psi}{\partial x}\right)_{y,z} + \left(\frac{\partial \psi}{\partial y}\right)_{x,z}\left(\frac{\partial y}{\partial x}\right)_{\psi,z} \tag{A.21}$$

in which the symbol $(\partial y/\partial x)_{\psi,z}$ appropriately indicates that the implied functional relation between y and x is that determined by the constancy of ψ and z. Equation A.21 can be written in the convenient form

$$\left(\frac{\partial y}{\partial x}\right)_{\psi,z} = \frac{-(\partial\psi/\partial x)_{y,z}}{(\partial\psi/\partial y)_{x,z}} \tag{A.22}$$

This equation plays a very prominent role in thermodynamic calculations. By successively putting $dy = 0$ and $dx = 0$ in equation A.20, we find the two similar relations

$$\left(\frac{\partial z}{\partial x}\right)_{\psi,y} = \frac{-(\partial\psi/\partial x)_{y,z}}{(\partial\psi/\partial z)_{x,y}} \tag{A.23}$$

and

$$\left(\frac{\partial z}{\partial y}\right)_{\psi,x} = \frac{-(\partial\psi/\partial y)_{x,z}}{(\partial\psi/\partial z)_{x,y}} \tag{A.24}$$

Returning to equation A.20 we again put $dz = 0$, but we now divide through by dy rather than by dx

$$0 = \left(\frac{\partial \psi}{\partial x}\right)_{y,z}\left(\frac{\partial x}{\partial y}\right)_{\psi,z} + \left(\frac{\partial \psi}{\partial y}\right)_{x,z} \tag{A.25}$$

whence

$$\left(\frac{\partial x}{\partial y}\right)_{\psi,z} = \frac{-(\partial\psi/\partial y)_{x,z}}{(\partial\psi/\partial x)_{y,z}} \tag{A.26}$$

and, on comparison with equation A.21, we find the very reasonable result that

$$\left(\frac{\partial x}{\partial y}\right)_{\psi,z} = \frac{1}{(\partial y/\partial x)_{\psi,z}} \tag{A.27}$$

From equations A.22 to A.24 we then find

$$\left(\frac{\partial x}{\partial y}\right)_{\psi,z}\left(\frac{\partial y}{\partial z}\right)_{\psi,x}\left(\frac{\partial z}{\partial x}\right)_{\psi,y} = -1 \tag{A.28}$$

Finally we return to our basic equation, which defines the differential $d\psi$, and consider the case in which x, y, and z are themselves functions of a variable u (as in equation A.12)

$$d\psi = \left[\left(\frac{\partial \psi}{\partial x}\right)_{y,z}\frac{dx}{du} + \left(\frac{\partial \psi}{\partial y}\right)_{x,z}\frac{dy}{du} + \left(\frac{\partial \psi}{\partial z}\right)_{x,y}\frac{dz}{du}\right]du \tag{A.29}$$

If ψ is to be constant, there must be a relation among x, y, and z, hence also among dx/du, dy/du, and dz/du. We find

$$0 = \left(\frac{\partial \psi}{\partial x}\right)_{y,z}\left(\frac{dx}{du}\right)_{\psi} + \left(\frac{\partial \psi}{\partial y}\right)_{x,z}\left(\frac{dy}{du}\right)_{\psi} + \left(\frac{\partial \psi}{\partial z}\right)_{x,y}\left(\frac{dz}{du}\right)_{\psi} \tag{A.30}$$

If we further require that z shall be a constant independent of u we find

$$0 = \left(\frac{\partial \psi}{\partial x}\right)_{y,z}\left(\frac{\partial x}{\partial u}\right)_{\psi,z} + \left(\frac{\partial \psi}{\partial y}\right)_{x,z}\left(\frac{\partial y}{\partial u}\right)_{\psi,z} \tag{A.31}$$

or

$$\frac{(\partial y/\partial u)_{\psi,z}}{(\partial x/\partial u)_{\psi,z}} = -\frac{(\partial \psi/\partial x)_{y,z}}{(\partial \psi/\partial y)_{x,z}} \tag{A.32}$$

Comparison with equation A.22 shows that

$$\left(\frac{\partial y}{\partial x}\right)_{\psi,z} = \frac{(\partial y/\partial u)_{\psi,z}}{(\partial x/\partial u)_{\psi,z}} \tag{A.33}$$

Equations A.22, A.27, and A.33 are among the most useful formal manipulations in thermodynamic calculations.

APPENDIX B

MAGNETIC SYSTEMS

If matter is acted on by a magnetic field it generally develops a magnetic moment. A description of this magnetic property, and of its interaction with thermal and mechanical properties, requires the adoption of an additional extensive parameter. This additional extensive parameter X and its corresponding intensive parameter P are to be chosen so that the *magnetic work* $đW_{\text{mag}}$ is

$$đW_{\text{mag}} = P\,dX \tag{B.1}$$

where

$$dU = đQ + đW_M + đW_c + đW_{\text{mag}} \tag{B.2}$$

Here $đQ$ is the heat $T\,dS$, $đW_M$ is the mechanical work (e.g., $-P\,dV$), and $đW_c$ is the chemical work $\Sigma \mu_j\,dN_j$. We consider a specific situation that clearly indicates the appropriate choice of parameters X and P.

Consider a solenoid, or coil, as shown in Fig. B.1. The wire of which the solenoid is wound is assumed to have zero electrical resistance (superconducting). A battery is connected to the solenoid, and the electromotive force (emf) of the battery is adjustable at will. The thermodynamic system is inside the solenoid, and the solenoid is enclosed within an adiabatic wall.

If no changes occur within the system, and if the current I is constant, the battery need supply no emf because of the perfect conductivity of the wire.

Let the current be I and let the local magnetization of the thermodynamic system be $\mathbf{M}(\mathbf{r})$. The current I can be altered at will by controlling the battery emf. The magnetization $\mathbf{M}(\mathbf{r})$ then will change also. We assume that the magnetization at any position $\mathbf{r}$ is a single-valued function of the current

$$\mathbf{M}(\mathbf{r}) = \mathbf{M}(\mathbf{r}; I) \tag{B.3}$$