A1. EXACT AND INEXACT DIFFERENTIALS

This chapter presents a brief discussion of exact and inexact differentials.

A1.0 Contents

A1.1 The Equation of Integrability

Consider a thermodynamic function, $U = U(S, V)$, where U and S are functions of state. The total differential, dU, is then an exact differential. To show this, we set

$$dU = X(S, V)\,dS + Y(S, V)\,dV \tag{A1.1$_1$}$$

where

$$X(S, V) = \left.\frac{\partial U}{\partial S}\right|_V \qquad \text{and} \qquad Y(S, V) = \left.\frac{\partial U}{\partial V}\right|_S. \tag{A1.1$_2$}$$

Now, if dU is an exact differential as asserted, mixed derivatives do not depend on the order of differentiation. Thus

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}, \tag{A1.1$_3$}$$

and it further follows that

$$\left.\frac{\partial X(S, V)}{\partial V}\right|_S = \left.\frac{\partial Y(S, V)}{\partial S}\right|_V. \tag{A1.1$_4$}$$

The last equation is the *equation of integrability*. It must be satisfied, as it is here, for the differential dU to be an exact differential. It thus constitutes a test for the exactness of a differential.

A1.2 The Exact Differential

Let us test the relation

$$dU = TdS - PdV \tag{A1.2$_1$}$$

for exactness. We now have $X(S,V) = T$, and $Y(S,V) = -P$, and thus Eq.(A1.1)$_4$ becomes

$$\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial P}{\partial S}\right|_V. \tag{A1.2$_2$}$$

But this is the first of the Maxwell relations, Eq.(10.6)$_1$, asserting that mixed derivatives do not depend on the order of differentiation. Thus the equation of integrability is satisfied.

A1.3 The Inexact Differential

Now consider the differential $dU = dQ + dW$ where $dW = -PdV$ and neither Q nor W are functions of state. We wish to ascertain if

$$dQ = dU + PdV \tag{A1.3$_1$}$$

is an *exact* differential. To subject it to the test of Eq.(A1.4), we first express dU in the form

$$dU = \left.\frac{\partial U}{\partial S}\right|_V dS + \left.\frac{\partial U}{\partial V}\right|_S dV \tag{A1.3$_2$}$$

and then substitute this into $dQ = dU + PdV$. The substitution yields

$$dQ = \left.\frac{\partial U}{\partial S}\right|_V dS + \left[\left.\frac{\partial U}{\partial V}\right|_S + P\right] dV \tag{A1.3$_3$}$$

and comparison with Eq.(A1.1)$_1$ shows that

$$X(S,V) = \left.\frac{\partial U}{\partial S}\right|_V \tag{A1.3$_4$}$$

while

$$Y(S,V) = \left.\frac{\partial U}{\partial V}\right|_S + P. \tag{A1.3$_5$}$$

Thus

$$\left.\frac{\partial X}{\partial V}\right|_S = \frac{\partial^2 U}{\partial V \partial S} \tag{A1.3$_6$}$$

and

$$\left.\frac{\partial Y}{\partial S}\right|_V = \frac{\partial^2 U}{\partial S \partial V} + \left.\frac{\partial P}{\partial S}\right|_V . \tag{A1.3$_7$}$$

Clearly, the equation of integrability is not satisfied and dQ is therefore an *inexact* differential. To emphasize this distinction inexact differentials are written in this text as δQ, δW, δM, etc., instead of dQ, dW, and dM, etc.